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MATHEMATICS

On a Stochastic Model of a Cascade

by

K. URBANIK

Presented by H. STEINHAUS on May 30, 1955

I. Let us take a physical cascade in a homogeneous medium composed of particles of a unique kind (e. g. a nucleon cascade), in which the destroying of particles is a random process. From the physical point of view it is assumed that:

(i) the future of a particle does not depend on its past but exclusively on its present state;

(ii) the fate of a particle and of its progenitors does not depend on what happens to other existent particles.

A cascade is usually treated as a homogeneous stochastic Markoff process $\langle \Omega, B_\Omega, Pr \rangle$ (cf. e. g. Kolmogoroff and Dmitrieff [2], Feller [1]). Here Ω is a space of non-negative integral-valued functions ω, defined for $t \geqslant 0$ (describing the number of particles at the moment t), having unilateral limits for every $t \geqslant 0$. B_Ω is the σ-field of sets spanned by the sets of the form:

$$A(t,n) = \{\omega : \omega \in \Omega, \omega(t) = n\}.$$

The transition probabilities

$$P_n^k(t) = Pr\{\omega(t) = k | \omega(0) = n\},$$

which satisfy the conditions of the transition probabilities of the homogeneous Markoff process, also satisfy

$$P_0^k(t) = \delta_0^k \qquad (k = 0,1,\ldots),$$

$$P_n^k(t) = \sum \prod_{i=1}^{n} P_1^{k_i}(t) \qquad (k = 0,1,\ldots;\ n = 1,2,\ldots), \tag{1}$$

where the indices k_i run over all systems of the non-negative integers $k_1 + \ldots + k_n = k$. Condition (1) is equivalent to the following one:

$$a_n^k = n a_1^{k-n+1} \qquad (n,k = 0,1,\ldots), \tag{2}$$

where

$$a_n^k = \frac{d}{dt} P_n^k(t)\Big|_{t=+0}.$$

Evidently, in this model of a cascade we cannot speak about single particles, their fates etc. Thus, the conditions (i), (ii) have no direct interpretation here. Consequently in strict investigations of the cascade process, conditions (1) and (2) are treated as axioms. Professor E. Marczewski proposed a model of a cascade in which one can speak about single particles, their fates, etc. It is founded on intuitive conditions (i), (ii). Such a model is investigated in this paper.

II. Let Ξ be the set of all systems $\xi = \langle x_1, \ldots, x_n \rangle$, where $x_1 = 1$, $x_k = \langle i, j \rangle$ $(i = 1,2,\ldots,j;\ j \in J;\ k \geqslant 2)$, and J is the set of integers determining the number of particles generated by the destroying of a particle. Evidently from $j \in J$ follows $j \geqslant 2$. Let V be a set of functions v, which are defined on Ξ and assume as their values real positive numbers or the abstract element $\square$, such that:

(a) $v(\langle 1 \rangle) \neq \square$,

(b) if $v(\langle x_1, \ldots, x_n \rangle) = \square$, then $v(\langle x_1, \ldots, x_n, x_{n+1} \rangle) = \square$,

(c) if $v(\langle x_1, \ldots, x_n \rangle) \neq \square$, then $v(\langle x_1, \ldots, x_n, x_{n+1} \rangle) = \square$
or $v(\langle x_1, \ldots, x_n, x_{n+1} \rangle) > v(\langle x_1, \ldots, x_n \rangle)$,

(d) if $v(\langle x_1, \ldots, x_n, \langle i, j \rangle \rangle) \neq \square$, then for $k = 1,2,\ldots,j$
$v(\langle x_1, \ldots, x_n \langle k, j \rangle \rangle) \neq \square$ and for $s = 1,2,\ldots,m;\ m \neq j$
$v(\langle x_1, \ldots, x_n \langle s, m \rangle \rangle) = \square$,

(e) if $v(\langle x_1, \ldots, x_n \rangle) \neq \square$ for $n = 1,2,\ldots,$ then
$$\lim_{n \to \infty} v(\langle x_1, \ldots, x_n \rangle) = \infty.$$

The function v describes the fate of all particles in the cascade. The intuitive sense of v is the following:

1^0 the equality $v(\langle x_1, \ldots, x_n \rangle) = t > 0$ holds, if the particle generated by a particle splitting into j_2 parts $(x_2 = \langle i_2, j_2 \rangle$; i_2 denotes the index distinguishing the j_2 parts) and j_3 parts, etc. vanishes at the moment t, i. e. is either destroyed or absorbed by the medium.

2^0 the equality $v(\langle x_1, \ldots, x_n \rangle) = \square$ holds, if there are no particles in the cascade generated by one particle at the initial moment $(x_1 = 1)$, by its splitting first into j_2 parts $(x_2 = \langle i_2, j_2 \rangle)$, then into j_3 parts $(x_3 = \langle i_3, j_3 \rangle)$, etc.

Let B_v be the σ-field of sets spanned by all the sets of the form:

$$B(\xi, t) = \{v : v \in V, v(\xi) < t\}, \qquad B(\xi) = \{v : v \in V, v(\xi) = \square\}.$$

The set $\{v : v \in V, v(\xi) \in U\}$ will be denoted briefly by $v(\xi) \in U$. If $\xi = \langle x_1, \ldots, x_n \rangle$ and $\eta = \langle x_1, \ldots, x_n, y_1, \ldots, y_m \rangle$ we write $\eta \in K(\xi)$ and $\eta - \xi = \langle 1, y_1, \ldots; y_m \rangle$. $K(\xi)$ is the cascade generated by the particle ξ.

Let P be a probability measure in B_V generating the conditional probability which satisfies

(I) $$P\{\bigcap_{\eta\in K(\xi)} v(\eta)\in U_\eta | v(\xi)\in U_\xi\}=P\{\bigcap_{\eta\in K(\xi)} v(\eta-\xi)\in U_\eta | v(\langle 1\rangle)\in U_\xi\},$$

(II) $$P\{\bigcap_{\eta\in K(\xi)} v(\eta)\in U_\eta | v(\xi)\in U_\xi, \bigcap_{a\in \Xi-K(\xi)} v(a)\in U_a\}=$$
$$=P\{\bigcap_{\eta\in K(\xi)} v(\eta)\in U_\eta | v(\xi)\in U_\xi\},$$

(III) $$P\{\bigcap_{\eta\in K(\xi)} v(\eta)\in U_\eta | v(\xi)\in U_\xi\}=P\{\bigcap_{\eta\in K(\xi)} v(\eta)\in T_t U_\eta | v(\xi)\in T_t U_\xi\},$$

where the sets $U_\eta(\eta\in\Xi)$ are either intervals of the positive halfline, or the one-point sets ($\square$) and

$$T_t U_\eta=\begin{cases}\{u-t: u\in U_\eta\} & \text{for} \quad U_\eta\subset[0,\infty)\\ (\square) & \text{for} \quad U_\eta=(\square).\end{cases}$$

In condition (III) we assume that $T_t U_\eta\subset[0,\infty)\cup(\square)$.

A system $\langle V,B_V,P\rangle$ is called a *cascade process*. Conditions (I), (II) are transcription of the conditions (i), (ii), and (III) is the condition of homogeneity of the medium.

Let us denote by ξ^*, for every $\xi=\langle x_1,\ldots,x_n\rangle$ $(n\geqslant 2)$, the system $\langle x_1,\ldots,x_{n-1}\rangle$. Let $\chi(v,t,\xi)$ be a characteristic function of the interval $[v(\xi^*),v(\xi))$ (here we assume $v(\langle 1\rangle^*)=0$ and that, if at least one of the end-points of the interval is equal to $\square$, this interval is empty). We now define the transformation of the space V into the space of all non-negative integral-valued functions defined for $t\geqslant 0$:

$$\Omega(v)=\omega(v,.)=\sum_{\xi\in\Xi}\chi(v,.,\xi).$$

The function $\omega(v,t)$ determines the number of particles at the moment t in the cascade v. Ω transforms $\langle V,B_V,P\rangle$ into $\langle\Omega(V),B_{\Omega(V)},\Omega P\rangle$. The following theorems, giving the relations between the above models of the cascade, have been proved:

THEOREM 1. *If $\langle V,B_V,P\rangle$ is a cascade process, then $\langle\Omega(V),B_{\Omega(V)},\Omega P\rangle$ is a homogeneous Markoff process satisfying* (1).

THEOREM 2. *If $\langle\Omega,B_\Omega,Pr\rangle$ is a homogeneous Markoff process satisfying* (1), *there is a cascade process $\langle V,B_V,P\rangle$ such that*

$$\langle\Omega,B_\Omega,Pr\rangle=\langle\Omega(V),B_{\Omega(V)},\Omega P\rangle.$$

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REFERENCES

[1] W. Feller, *On the theory of stochastic processes, with particular reference to applications*, Proc. Berkeley Symp. Math. Statistics and Probability 1949, 403-432.

[2] A. N. Kolmogoroff and N. A. Dmitrieff, *Vietviashtchiiesia slutchainyie protsessy*, Dokl. Akad. Nauk SSSR **56** (1947), 7.

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THEORETICAL PHYSICS

Co-variant One-Time Formulation of the Many-Body Problem in the Quantum Theory

by

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Presented by W. RUBINOWICZ on May 20, 1955

A co-variant one-time formulation of the many-body problem in the quantum field theory is obtained by transforming the conventional many-time equations of this problem into other equivalent equations which relate only those values of the wave function and its derivatives which correspond to one space-like hypersurface σ. The transformation is carried out for arbitrary values of the coupling constant λ with the exception of certain characteristic values λ_k. For small values of λ explicit expressions are given for the kernels of the one-time equations by means of expansions in powers of λ. These kernels are uniquely determined by the kernels of the original many-time equations. In the absence of external forces, the kernels of the one-time equations are independent of the time variable. These equations may be solved, therefore, by means of the stationary perturbation methods in contradistinction to the original many-time equations which do not admit of stationary treatment.

1. Introduction. Many important problems in theoretical physics are formulated in terms of integro-differential equations. In particular, the basic equations of the theory of bound states and of the non-local theory of elementary particles are partial integro-differential equations in Minkowski's space containing integrals over *four-dimensional* regions of space-time. These equations provide us with a *many-time* description of physical events in the sense that they relate values of the unknown functions and their derivatives corresponding to different values of the time variable. The question arises as to whether it is possible to construct a *three-dimensional* mathematical formalism providing an equivalent co-variant *one-time* description of these phenomena. Such a one-time description could be of importance not only for the development of the theory but also for the practical determination of the solutions. Therefore, several authors (Sal-

peter [1], Lévy [2], Macke [3], Klein [4], and quite recently Kurşunoğlu [5], have investigated the problem of reducing the four-dimensional formalism for bound states (of Schwinger [6], Bethe and Salpeter [7], and Günther [8]) to the three-dimensional one, and of connecting the latter with the three-dimensional Tamm-Dancoff formalism. (The old one of Lévy [2], Klein [9], Cini [10] and the new one of Dyson [11], and Taylor [12]).

The effective calculations were based on the assumption of a certain kind of separability of the relative-time or relative-energy dependence in the four-dimensional wave function, which assumption was only approximately true. Moreover, the relation between the four-dimensional and three-dimensional wave functions did not, in general, allow of any clear interpretation. It was even emphasised (Klein [4]) that in general an exact co-variant one-time formulation of a many-time theory (described by integro-differential equations) is impossible. We have proved that a co-variant partial integro-differential equation in Minkowski's space may always be replaced by another *equivalent* co-variant integro-differential equation containing surface integrals over one space-like surface σ only. These surface integrals are independent of the particular position of σ in the domain under consideration and, therefore, may be chosen in such a way that the resulting equation relates only those values of the unknown functions and their derivatives which correspond to points situated on the same surface. Such an equation yields obviously a one-time formulation of the theory, the surface σ being a relativistically invariant generalization of the conception of time.

The proof of this equivalence theorem may be carried out for a wide class of integro-differential equations. To avoid unessential complications, however, we shall confine ourselves to the consideration of one particular type of equations, namely, those describing a system of two particles with spin 1/2, interacting by means of a Bose-field. These equations are of particular importance for the theory of bound states. Considerations concerning this same problem in the non-local theories of elementary particles are published elsewhere (Rzewuski [13]). How the three-dimensional formalism presented in this paper is related to the new Tamm-Dancoff formalism (Dyson [11]) is an open question.

2. Equivalence theorem. Consider the system of two integro-differential equations

$$(2.1)\qquad (\underset{\sim}{\partial}^{(i)}+\varkappa^{(i)})\psi(x_1,x_2)=\lambda\int_{\sigma_I}^{\sigma_{II}}\int G^{(i)}(x_1,x_2;x_1',x_2')\,\psi(x_1,x_2)\,dx_1'dx_2' \qquad (i=1,2),$$

where

$$\underset{\sim}{\partial}^{(i)}=\gamma_\mu\partial_\mu^{(i)},$$
$$(\gamma_\mu^{(i)})=(-i\beta^{(i)}\vec{\alpha}^{(i)},\beta^{(i)}),$$
$$\partial_\mu^{(i)}=\frac{\partial}{\partial x_\mu^{(i)}},$$

and the unknown function ψ is a function of the two points x_1 and x_2 in Minkowski's space with co-ordinates $x_\mu^{(1)}$ and $x_\mu^{(2)}/(x_\mu^{(i)}) = (\vec{x}_i, ict_i)/$; dx_1 and dx_2 are four-dimensional elements of volume around these points and the integration is carried out over a domain Ω of space-time contained between two fixed space-like hypersurfaces σ_I and σ_{II} *). The kernels $G^{(i)}$ of equations (2.1) are given functions of four points. In the case of spin $\frac{1}{2}$, ψ is a second-rank bispinor and $G^{(i)}$ are fourth-rank bispinors. λ and $\varkappa^{(i)}$ $(i=1,2)$ are parameters.

Equations of type (2.1) are used for the determination of the wave function $\psi(x_1, x_2)$ in the configurational space of two fermions interacting by means of a Bose-field (cf. Bethe and Salpeter [7], Günther [8]).

We have proved the following equivalence theorem, the proof of which will be published elsewhere: the system (2.1) of consistent integro-differential equations is equivalent to the system

$$(\Box^{(i)} + \varkappa^{(i)})\psi(x_1, x_2) = \tag{2.2}$$
$$= \lambda \int_{\sigma_1}\int_{\sigma_2} A^{(i)}[\sigma_1, \sigma_2](x_1, x_2; x_1', x_2')\gamma_\mu^{(1)}\gamma_\nu^{(2)}\psi(x_1', x_2')\, d\sigma_\mu^{(1)}\, d\sigma_\nu^{(2)} \qquad (i=1,2),$$

for x_1 and x_2 inside Ω, and if the following conditions are satisfied:

1. The kernels $G^{(i)}$ admit unique solutions of equations (2.1) and

$$A^{(i)}[\sigma_1, \sigma_2](x_1, x_2; x_1', x_2') =$$
$$= \{G^{(i)} S\}(x_1, x_2; x_1', x_2') + \lambda \{G^{(i)} RS\}(x_1, x_2; x_1', x_2') + \tag{2.3}$$
$$+ \lambda \int_{\sigma_1}\int_{\sigma_2} A^{(i)}[\sigma_1, \sigma_2](x_1, x_2; x_1'', x_2'')\gamma_\mu^{(1)}\gamma_\nu^{(2)}\{RS\}(x_1'', x_2''; x_1' x_2')\, d\sigma_\mu^{(1)''}\, d\sigma_\nu^{(2)''} \quad (i=1,2),$$

where $R(x_1, x_2; x_1', x_2')$ is the resolving kernel of the integral equation equivalent to (2.1) and

$$S(x_1, x_2; x_1', x_2') = S^{(1)}(x_1 - x_1')\, S^{(2)}(x_2 - x_2') \tag{2.4}$$

is defined in terms of the well-known Jordan-Pauli singular function $\Delta_\varkappa(x)$, corresponding to $\varkappa^{(1)}$ and $\varkappa^{(2)}$ respectively,

$$S^{(i)}(x) = (\Box - \varkappa^{(i)})\Delta_{\varkappa^{(i)}}(x) \qquad (i=1,2). \tag{2.5}$$

The symbols $\{A\,B \ldots C\}(x_1, x_2; x_1', x_2')$ occurring in (2.3) denote convolutions of the functions inside the brackets,

$$\{A\,B \ldots C\}(x_1, x_2; x_1', x_2') \equiv$$
$$\equiv \int_{\sigma_I}^{\sigma_{II}} \ldots \int_{\sigma_I}^{\sigma_{II}} A(x_1, x_2; \xi_1, \xi_2)\, d\xi_1\, d\xi_2 B(\xi_1, \xi_2, \ldots) \ldots C(\ldots; x_1', x_2'). \tag{2.6}$$

*) The considerations in this paper make no use of the finiteness of the integration domain Ω. Thus, in particular, we may also consider equations of the type (2.1) containing integrals over the whole of space-time, i. e. we may remove in (2.1) σ_I and σ_{II} into $-\infty$ and $+\infty$ respectively.

2. λ does not belong to the spectrum of characteristic values of the equations.

For the one-time formulation of the theory it is important to note that — as may be demonstrated — the right-hand side of equations (2.2) does not depend on σ_1 and σ_2. The said result gives us a free choice as regards the surfaces σ_1 and σ_2 in equations (2.2). Assuming now that the points x_1 and x_2 on the left-hand side of these equations are space-like (in this case only a statistical interpretation of the function $\psi(x_1, x_2)$ is possible) we may choose σ_1 to coincide with σ_2 and to pass through those points. Equations (2.2) now take the form:

$$(\hat{\varrho}^{(i)} + \varkappa^{(i)})\psi(x_1, x_2) = \tag{2.7}$$
$$= \lambda \int_{\sigma} \int_{\sigma} A^{(i)}[\sigma, \sigma](x_1, x_2; x_1', x_2') \gamma_{\mu}^{(1)} \gamma_{\nu}^{(2)} \psi(x_1', x_2') d\sigma_{\mu}^{(1)'} d\sigma_{\nu}^{(2)'} \quad (i = 1, 2),$$

where σ is an arbitrary space-like surface passing through x_1 and x_2.

The above considerations may be extended immediately to the general case of the n-body problem as formulated by Günther [8].

3. Calculations of the kernels $A^{(i)}$ for small values of λ. For practical purpose it is important to express the kernels $A^{(i)}[\sigma_1, \sigma_2](x_1, x_2; x_1', x_2')$ of equations (2.7) or (2.2) explicitly by means of the kernels $G^{(i)}(x_1, x_2; x_1', x_2')$ of the original equation (2.1). This is possible e. g. for those values of the parametr λ which admit convergent expansions of the quantities $G^{(i)}, A^{(i)}$ and R in powers of λ *)

$$G^{(i)} = \sum_{n=0}^{\infty} \lambda^n G_n^{(i)}, \qquad A^{(i)} = \sum_{n=0}^{\infty} \lambda^n A_n^{(i)} \qquad R = \sum_{n=0}^{\infty} \lambda^n R_n \qquad (i = 1, 2). \tag{3.1}$$

Introducing (3.1) into (2.3) and equating the coefficients in terms containing equal powers of λ, we get the following recurrence formulae for the quantities $A_n^{(i)}$ $(i = 1, 2)$ **):

$$A_n^{(i)}[\sigma_1, \sigma_2](x_1, x_2; x_1', x_2') =$$
$$= \{G_n^{(i)} S\}(x_1, x_2; x_1', x_2') + \sum_{m=0}^{n-1} \{G_n^{(i)} R_{n-m-1} S\}(x_1, x_2; x_1', x_2') + \tag{3.2}$$
$$- \sum_{m=0}^{n-1} \int_{\sigma_1} \int_{\sigma_2} A_m^{(i)}[\sigma_1, \sigma_2](x_1, x_2; x_1'', x_2'') \gamma_{\mu}^{(1)} \gamma_{\nu}^{(2)} \{R_{n-m-1} S\}(x_1'', x_2''; x_1', x_2') d\sigma_{\mu}^{(1)''} d\sigma_{\nu}^{(2)''}$$
$$(i = 1, 2; \; n = 0, 1, 2, \ldots),$$

where the expansion coefficients R_n of R may be expressed by $G_m^{(i)}$.

*) So far, the only effective presentation given of the kernels $G^{(i)}$ is the one in the form of expansion series in powers of the coupling constant λ.

**) The convention used here is that, for $n = 0$, $\sum_{m=0}^{n=1} = 0$.

4. Final remarks. In view of the one-time equations (2.7) we are particularly interested in the form of $A^{(i)}[\sigma_1,\sigma_2](x_1,x_2;x_1',x_2')$ in the case when $\sigma_1=\sigma_2=\sigma$ and when both x_1,x_2 and x_1',x_2' are situated on σ.

Choosing for σ the plane surface $t=$ const. we have, according to (3.2), the result that $A^{(i)}$ is a function of one time t only. Denoting the first three co-ordinates of the points x_1 and x_2 by $\bar{x}_1$ and $\bar{x}_2$ we may write this explicitly:

$$A^{(i)}=A^{(i)}[t](\bar{x}_1,\bar{x}_2;\bar{x}_1',\bar{x}_2';t). \tag{4.1}$$

Multiplying equations (2.7) by $\hbar c\gamma_4^{(1)}$ and $\hbar c\gamma_4^{(2)}$ respectively, adding the resulting equations and using (4.1), we may write the one-time equations for the two-particle problem in the form of a Schrödinger equation

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi(\bar{x}_1,\bar{x}_2;t)&=(H^{(1)}+H^{(2)})\psi(\bar{x}_1,\bar{x}_2;t)+\\ &+\int_v\int V(\bar{x}_1,\bar{x}_2;\bar{x}_1',\bar{x}_2';t)\psi(\bar{x}_1',\bar{x}_2';t)\,dv_1'dv_2', \end{aligned} \tag{4.2}$$

$$\begin{aligned} V(\bar{x}_1,\bar{x}_2;\bar{x}_1',\bar{x}_2';t)&=\\ =\lambda\hbar c[\gamma_4^{(1)}A^{(1)}[t](\bar{x}_1,\bar{x}_2;\bar{x}_1',\bar{x}_2';t)&+\gamma_4^{(2)}A^{(2)}[t](\bar{x}_1,\bar{x}_2;\bar{x}_1',\bar{x}_2';t)]\gamma_4^{(1)}\gamma_4^{(2)}, \end{aligned}$$

where

$$H^{(i)}=\gamma_4^{(i)}[\hbar c\bar{\gamma}^{(i)}\bar{\partial}^{(i)}+m^{(i)}c^2]=-i\hbar c\bar{\alpha}^{(i)}\bar{\partial}^{(i)}+\beta^{(i)}m^{(i)}c^2 \qquad (i=1,2) \tag{4.3}$$

are the free Hamiltonians of the two particles, $\bar{\gamma}=(\gamma_1,\gamma_2,\gamma_3)$ $\bar{\partial}=(\partial_1,\partial_2,\partial_3)$, $dv=dxdydz=id\sigma_4$, $m=\dfrac{\hbar\varkappa}{c}$ and v is the domain under consideration.

The interaction term in the Hamiltonian (4.2) is an integral operator operating on the variables $\bar{x}_1$ and $\bar{x}_2$. In the case when the system under consideration is not acted upon by external forces the kernels of the original equations (2.1) may depend on x_1,x_2,x_1',x_2' only by means of the co-ordinate differences. This is necessary to secure translational invariance. In this case the kernels $A^{(i)}$ depend also only on co-ordinate differences (cf. (3.2)) and the kernel of equation (4.2) becomes time-independent *):

$$A^{(i)}=A^{(i)}(\bar{x}_1,\bar{x}_2;\bar{x}_1',\bar{x}_2'). \tag{4.4}$$

This is an advantage of the one-time formulation as compared with the many-time one (2.1) viz., that it admits the application of stationary methods. Assuming the solution (4.2) in the form

$$\psi(\bar{x}_1,\bar{x}_2;t)=\varphi(\bar{x}_1,\bar{x}_2)e^{-\frac{i}{\hbar}Et} \tag{4.5}$$

*) More generally, this kernel is time-independent when external forces do not depend on time (invariance for time translation).

we get the stationary Schrödinger equation

$$E\varphi(\bar{x}_1,\bar{x}_2)=(H^{(1)}+H^{(2)})\varphi(\bar{x}_1,\bar{x}_2)+\int_v\int V(\bar{x}_1,\bar{x}_2;\bar{x}_1',\bar{x}_2')\varphi(\bar{x}_1',\bar{x}_2')\,dv_1'dv_2',$$

$$V(\bar{x}_1,\bar{x}_2;\bar{x}_1',\bar{x}_2')=\lambda\hbar c[\gamma_4^{(1)}A^{(1)}(\bar{x}_1,\bar{x}_2;\bar{x}_1',\bar{x}_2')+\gamma_4^{(2)}A^{(2)}(\bar{x}_1,\bar{x}_2;\bar{x}_1',,\bar{x}_2')]\gamma_4^{(1)}\gamma_4^{(2)}, \tag{4.6}$$

to which e. g. the conventional stationary perturbation method may be applied. As the unperturbed Hamiltonian, one may use any energy observable with known eigenstates and closely approximating the total energy of the system. Generally, for bound states, the free Hamiltonian $H^{(1)}+H^{(2)}$ cannot be successfully used as the unperturbed Hamiltonian. The interaction term in the equation (4.6) does not depend on the energy E and differs in this respect from the interaction term obtained by the Tamm-Dancoff method (cf. Klein [14], Taylor [15]).

It should be noted that the above considerations may be carried out also in an evidently co-variant way by means of an appropriate parametrisation of the surfaces σ.

Equations (4.2), as well as (2.7), are equivalent to the original equations (2.1) whenever we consider exact solutions. However, in practical calculations one always uses an approximation method. It is obvious from the above considerations that if in the kernels of (2.1) and also in the kernel of (4.2) we retain only terms up to the order n in the coupling constant λ and then solve the resulting equations exactly, the solutions will, in general, differ by terms of the order $n+1$. This difference becomes essential when expansions of solutions in powers of λ are slowly convergent (or divergent) as they usually are for bound states. In the case of equations (2.1) one may try to retain in the kernels

$$G^{(i)}=\sum_{n=0}^{\infty}\lambda^n G_n^{(i)}$$

only the lowest term $G_0^{(i)}$ (the lowest "ladder approximation", cf. Bethe and Salpeter [7]) and then solve the approximate equations exactly (Günther [16]). The one-time equation (4.2) (or (2.7)) corresponding exactly to these approximate equations will, in general, possess a kernel which is an expansion in powers of λ. Now, one should neglect also in this expansion all higher order terms, as it would be inconsequent to retain in the kernel of (4.2) higher order terms generated by $G_0^{(i)}$ when terms of the same order, generated by $G_1^{(i)}$, etc. are not taken into account.

It is an open question whether the one-time or the many-time formulation is more practical for explicit calculations. It seems certain, however, that the results will differ essentially whenever an approximate treatment is applied. Calculations of energy levels in the two-body problem in electrodynamics (Salpeter [1], Karplus and Klein [17], Fulton and Martin [18]) seem to argue — in view of the formalism presented in this paper — for

that approximative treatment which consists in breaking off the kernel in the one-time equation rather than the kernels in the many-time equations. We note, however, that the procedure of breaking off the kernel in the one-time equations spoils its Lorentz invariance (its independence of σ) in which it differs from the breaking off the kernel in the many-time equations. After this procedure the one-time equation becomes only approximately independent of the hypersurface σ. We hope to come back to this question elsewhere.

The authors are indebted to Mr. M. Günther and Mr. J. Łopuszański for interesting discussion on this subject.

INSTITUTE OF PHYSICS, POLISH ACADEMY OF SCIENCES

REFERENCES

[1] E. E. Salpeter, Phys. Rev., **87** (1952), 328.
[2] M. Lévy, Phys. Rev., **88** (1952), 72, 725.
[3] W. Macke, Z. Naturforsch., **8a** (1953), 599, 615.
[4] A. Klein, Phys. Rev., **94** (1954), 1052.
[5] B. Kurşunouğlu, Phys. Rev., **96** (1954), 1690.
[6] J. Schwinger, Proc. Natl. Acad. Sci. U. S., **37** (1951), 452, 455.
[7] E. E. Salpeter and H. A. Bethe, Phys. Rev., **84** (1951), 1322.
[8] M. Günther, Phys. Rev., **88** (1952), 1411; **94** (1954), 1347.
[9] A. Klein, Phys. Rev., **90** (1953), 1101.
[10] M. Cini, Nuovo Cimento, **10** (1953), 526, 614.
[11] F. J. Dyson, Phys. Rev., **91** (1953), 1543.
[12] J. C. Taylor, Phys. Rev., **95** (1954), 1313.
[13] J. Rzewuski, Acta Phys. Pol., **13** (1954), 135; **14** (1955), 123.
[14] A. Klein, Phys. Rev., **94** (1954), 195.
[15] J. C. Taylor, Phys. Rev., **88** (1954), 1438.
[16] M. Günther, (1955) (unpublished).
[17] R. Karplus and A. Klein, Phys. Rev., **87** (1953), 848.
[18] T. Fulton and P. C. Martin, Phys. Rev., **95** (1954), 811.

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THEORETICAL PHYSICS

Repulsive Forces and the Problem of Saturation in the Nucleus

by
G. SZAMOSI

Presented by L. INFELD on June 8, 1955

The assumption of the existence of a repulsive interaction of very short range between the nucleons ($\sim 0.1b$ if b is the range of nuclear forces) was first formulated in 1951 [1]. This assumption, as is well known, was necessary in order to eliminate contradictions arising from the results of scattering experiments, on the one hand, and some data concerning composite nuclei on the other, such as charge independence.

The most important contradiction, perhaps, is that connected with the problem concerning the cause of saturation of binding energy. It is well-known that in order to explain this saturation it must be assumed that if the potential between two nucleons is given by

$$V_{ik} = (a + bP_r^{ik})J(r_{ik}), \tag{1}$$

where P_r^{ik} is the Majorana operator, $J(r_{ik})$ is the space-dependent part of the potential, and a and b are constants, then the following inequality must hold: $4a \leqslant b$ (see e. g., [2]). On the other hand, the scattering experiments performed during the last few years undoubtedly show that in reality $a \sim b$.

In principle then, it is quite obvious that the assumption of a repulsive interaction brings a solution of the saturation problem nearer, increasing, for instance, the kinetic energy of nucleons [3]. Pertinent calculations reveal that in the case of a Serber interaction an increase in the kinetic energy will only lead to saturation, assuming such a range of the repulsive forces as contradicts the results of the scattering experiments [4].

The results which follow from the classical relativistic theory of the motion of the particle in a "nuclear-force-like" field offer new points of view. Werle [5] was the first to show, using a nonrelativistic approximation, that owing to relativistic causes the sources of the field exert

a short-range, repulsive force upon a nucleon moving in an attractive scalar field (cf. too [6]). Later, it was successfully shown that this was a direct consequence of the exact relativistic equations of motion in scalar fields [7]. The elementary quantum-mechanical treatment of motion in pseudoscalar fields leads to the very same type of repulsion [8], [9], [10], [11].

Let us discuss the scalar field since it is the easiest to deal with. The physical situation pertaining to the problem is clear, and the assumptions to be used are acceptable in relativistic dynamics under very general conditions [12]. As has been shown [7], the apperance of a relativistic "equivalent potential" indicates, without any additional assumption, that there are classical three-body forces acting among the particles moving in the scalar field. More explicitly, when the field is generated by n nucleons the expression for the potential acting on a nucleon is

$$W(r)=\sum_{i=1}^{n}{}'\left[-\Phi(r-r_i)+\frac{1}{2mc^2}\Phi^2(r-r_i)+\sum_{k\neq i}^{n}\frac{1}{mc^2}\Phi(r-r_i)\Phi(r-r_k)\right],$$

where Φ is a static potential, the other symbols being the customary ones. It follows that, denoting the interaction between the pairs of nucleons by V_{ik}, the expression of the potential energy in a Hartree-Fock approximation is

$$(2)\quad E_p=\frac{1}{2}\sum_{i\neq 1}\int\psi_i^*(x_1)\psi_k^*(x_2)V_{ik}(x_1x_2)\begin{vmatrix}\psi_i(x_1)\psi_i(x_2)\\ \psi_k(x_1)\psi_k(x_2)\end{vmatrix}dx_1dx_2+$$

$$+\frac{1}{12mc^2}\sum_{i\neq k\neq j}\int\psi_i^*(x_1)\psi_k^*(x_2)\psi_j^*(x_3)V_{ik}(x_1x_2)V_{ij}(x_1x_3)\begin{vmatrix}\psi_i(x_1)\psi_i(x_2)\psi_i(x_3)\\ \psi_k(x_1)\psi_k(x_2)\psi_k(x_3)\\ \psi_j(x_1)\psi_j(x_2)\psi_j(x_3)\end{vmatrix}dx_1dx_2dx_3,$$

where the symbols ψ_i denote the individual wave functions of the x_i-space, spin, and charge co-ordinates, and where the integration contains summations with respect both to the spin and to the charge co-ordinates.

Accordingly, it can be seen that the non-linearity of the relativistic potential automatically gives rise to quantum-mechanical, many-body forces. From this it follows that the effect of the relativistic potential may be considerably greater than that of a repulsion introduced phenomenologically, or even than that resulting from treatment of the two-body problem.

The influence upon saturation of the three-body forces and of repulsion can be described as follows.

Let us calculate the binding energy of a sphere of radius R, homogeneously filled with nucleons; this energy is made up of potential energy and kinetic energy increased by repulsion. Thus we can write:

$$E=\frac{1}{2}\int\varrho\left(\Phi+\frac{1}{2mc^2}\Phi^2\right)dV+E_{kin},$$

where Φ is a solution of the Yukawa equation

$$\Delta\Phi - \mu^2\Phi = 3g\frac{A}{R^3}.$$

We get

$$E = -A^2g^2[\alpha_1 R^{-3} - \alpha_2 R^{-4}] + A^3g^4[\alpha_3 R^{-6} - \alpha_4 R^{-7} + \alpha_5 R^{-8} + \alpha_6 R^{-9}] + \\ + \frac{\alpha_7}{r_0^2}\int_0^A \log^{2/3}\left(1 - n\frac{r_0^3}{R^3}\right)dn,$$

where r_0 is the radius of the repulsive core [3] and the constants $\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6, \alpha_7$ can easily be calculated. As can easily be seen [13] there is no value of g (mesic charge) for which the above equation gives the correct dependence of the nuclear radius on A, which minimises the energy. From this it can be inferred that along with the three-body forces and repulsion the exchange forces certainly play a major rôle in the interpretation of saturation.

For this very reason, it does not seem superfluous to determine the ratio of a to b from the condition of saturation by the usual variation method. On account of the existence of three-body forces, the condition obtained for the ratio of a to b will depend on the mass number A. The calculations, which cannot be dealt with in detail here, reveal that the empirical condition, viz., that $a \sim b$, is practically fulfilled in respect of heavy nuclei. To fulfill this condition in every case imposes a condition on the effective nucleon mass. Thus by an entirely different route, we arrive at about the same value for the nucleon mass as that obtained by Brueckner and his co-workers [14].

A more detailed discussion of this problem will be published in Acta Physica Hungarica.

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REFERENCES

[1] R. Jastrow, Phys. Rev., **81** (1951), 165.
[2] W. Heisenberg and W. Macke, *Theorie des Atomkerns*, Göttingen, 1951.
[3] G. Szamosi, Naturwiss, **41** (1954), 369.
[4] — Magy. Fiz. Foly., **2** (1954), 313.
[5] J. Werle, Bull. Acad. Polon. Sci., Cl III, **1** (1953), 281.
[6] P. Kunins and I. Taksars, Litv. PSR Ak. Vest., **11** (1951), 1775.
[7] G. Szamosi and G. Marx, Acta Phys. Hung. **4** (1954), 219.
[8] P. Kunins and I. Taksars, Litv. PSR Ak. Vest., **8** (1952), 137.
[9] G. Marx, Fiz. Szemble, **4** (1954), 166.
[10] J. Werle, Nuovo Cimento, **1**, X (1955), 537.
[11] G. Györgyi, Acta Phys. Hung., **5** (1955), 119.
[12] G. Szamosi, Acta Phys. Hung., (to be published).
[13] G. Szamosi and M. Ziegler, KFKI Közl. 1955.
[14] K. A. Brueckner et al., Phys. Rev. **95** (1954), 217.

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A Simple Theory of the $^7Li(\gamma,{}^3H)^4He$ Reaction

by

W. CZYŻ

Presented by H. NIEWODNICZAŃSKI on June 3, 1955

The results of recent experimental investigations [1], [2], [3], [4] and [5] do not give a complete picture of the reaction $^7Li(\gamma,{}^3H)^4He$. Nevertheless, the following simple theory may make some contribution to the understanding of the mechanism of this reaction.

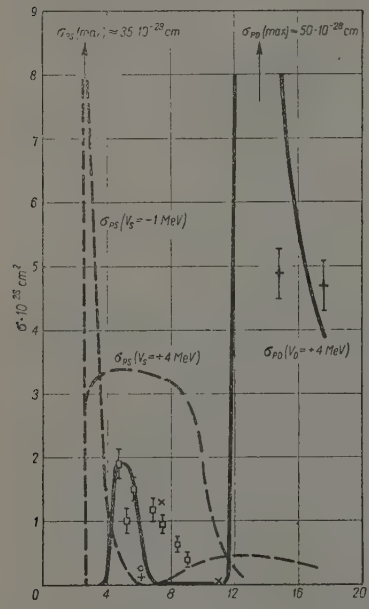
We assume a two-body model of the ^{7}Li-nucleus composed of a triton and an α-particle. This model is based on the following considerations:

1. The threshold energy of the $^7Li(\gamma,t)\alpha$ reaction is comparatively low (2.465 MeV), whereas the threshold energies for the (γ,n) and (γ,p) reactions are 7.15 MeV and 9.5 MeV, respectively.
2. It is known that the ground state of the ^{7}Li-nucleus is $P_{3/2}$. This state is easily obtainable from the t-α model.
3. A system composed of a triton (magnetic moment 2.9789) and α-particle (magnetic moment 0) possesses in its ground state $P_{3/2}$ (with orbital magnetic moment 0.405) a magnetic moment equal to 3.3839 nuclear magnetons. When compared with the experimental values of 3.2559 nuclear magnetons it shows a rather small difference of only 3.8%.

In the preliminary calculations we assume the interaction between the triton and the α-particle to be in the form of a square potential well with radius r_0 and depth V. V is a function of the orbital angular momentum of the t-α system. The Coulomb interaction between t and α is neglected. The most important transitions are the electric dipole ones $P \to S$ and $P \to D$. The cross-section σ_{PS} and σ_{PD} of the $^7Li(\gamma,t)\alpha$ reaction were evaluated in analogy with the calculations of Guth and Mullin [6]. Therefore we restrict ourselves to a discussion of the results presented in Fig. 1.

The values of σ_{PS} and σ_{PD}, for $r_0 = 5 \cdot 10^{-13}$ cm., $V_P = -8 \cdot 45$ MeV, $V_S = -1$ MeV and $+4$ MeV, $V_D = +4$ MeV (the indices indicate the angular momentum of the t-α system) are plotted against the γ-ray energy.

V_P is determined by the binding energy -2.465 MeV (for fixed r_0), V_S and V_D are adjusted to the experimental results [1], [2], [3], [4], and [5]. The angular distribution of tritons in the $P \rightarrow D$ transition may be represented by $1-0.414\cos^2\theta$, where θ is the angle between the direction of the outgoing triton and of that of the incident photon beam. The angular distribution of tritons in the $P \rightarrow S$ transition is isotropic.



□ Stoll (1954) + Titterton Brinkley (1953)
⊙ Nabholz, Stoll, Wäffler (1952)
× Stoll, Wächter (1953)

As shown by Stoll [2], the angular distribution for incident photons of energy 4.7 MeV is approximately proportional to $1-0.5\cos^2\theta$. It can be seen from Fig. 1 that the assumption of the same t-α interaction in the S- and D-states gives a wrong angular distribution for $\hbar\omega = 4.7$ MeV. Therefore, it seems correct to assume attraction between t and α in the S- state, and repulsion in the D-state. The assumption of attraction in the D-states leads to cross-sections being in complete disagreement with the experiment. The value $V_S = -1$ MeV was chosen, since already for $V_S = -1.2$ MeV we obtain a bound state of the t-α system which is not known for the ^{7}Li-nucleus. In the neighbourhood of the threshold energy for this reaction, σ_{PS} shows a sharp maximum. It may be supposed that the cross-section for γ-ray energy exceeding $\hbar\omega \approx 4$ MeV is determined mainly by the $P \rightarrow D$ transition.

We now go on to a consideration of some details concerning the shape of the cross-section curve in the energy regions $4\text{ MeV} \lesssim \hbar\omega \lesssim 10$ MeV and $\hbar\omega \lesssim 4$ MeV. In the region $4 \lesssim \hbar\omega < 10$ MeV, the results obtained by Stoll [2] indicate the existence of a few resonances not shown in Fig. 1. These resonances may be obtained in the model under consideration only from the magnetic dipole, the electric quadrupole and still higher multipole — transitions. It is doubtful though, whether in such a rough model these resonances can really be obtained. Nevertheless, we believe that the basic form of the cross-section is given by the $P \rightarrow D$ transition, and the mechanism of the reaction is sufficiently well described by the t-α model of the ^{7}Li-nucleus. We may suppose that besides this

"two-body mechanism" there exists another mechanism of the $^7\mathrm{Li}(\gamma,t)\alpha$ reaction (e. g. a compound nucleus mechanism), from which may be obtained the "fine structure" of the cross-section curve in the region $4 \lesssim \hbar\omega \lesssim 10$ MeV.

It seems that the experimental results of Stoll [1], [2] do not give a satisfactory answer to this question as to the cross-section for $\hbar\omega \lesssim 4$ MeV. This is probably due to the imperfection of the nuclear emulsion technique for studying the disintegration products of such small energies. $(E_t + E_a \lesssim 1.5$ MeV). If our model were valid for all γ-ray photons with energy above the threshold value (2.465 MeV), The $P \to S$ transition would give a sharp maximum in the neighbourhood of the reaction threshold. It is possible, however, that the pattern of the reaction cross-section in the energy domain $\hbar\omega \lesssim 4$ MeV may be considerably changed if the lifetime of the α particle in the ^{7}Li-nucleus is sufficiently short. For example, it may be supposed that the two constituents of ^{7}Li-nucleus cannot be distinguished from each other, since one proton is frequently exchanged between the triton and α-particle. If the lifetime of the α-particle (denoted by T) in the ^{7}Li-nucleus is shorter than the period of the electromagnetic vibrations of the incident photon, then for this photon the electric dipole moment of the ^{7}Li-nucleus will not exist and consequently neither will the electric dipole transitions. If we assume $T \lesssim 10^{-21}$ sec (the lower limit of Wheeler's estimation [7]), then the critical energy above which the electric dipole moment of the ^{7}Li-nucleus becomes important may be estimated as follows:

$$h\nu_{\mathrm{crit}} = \hbar\omega_{\mathrm{crit}} \approx 0.66 \cdot 10^{-21} \text{ MeV sec} \cdot 2\pi \cdot 10^{21} \text{ sec}^{-1} \approx 4 \text{ MeV}.$$

It is then possible that further measurements may give very small values of the cross-section for γ-ray energies $\hbar\omega \lesssim 4$ MeV.

In addition, measurements of the angular distribution of tritons for γ-ray energies $14 \text{ MeV} \lesssim \hbar\omega \lesssim 18$ MeV might give valuable information concerning the mechanism of the $^7\mathrm{Li}(\gamma,t)\alpha$ reaction. We hope that these experiments will confirm the distribution $1 - 0.414 \cos^2\theta$ suggested in the present note, which is characteristic for the $P \to D$ transition.

The proper magnitude of the Coulomb corrections which have so far been neglected, is still not known to the author of this note.

A more complete report of the present investigations will be published in Acta Physica Polonica.

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REFERENCES

[1] P. Erdös, P. Stoll, M. Wächter, V. Wataghin, Nuovo Cimento **12** (1954), 639.
[2] P. Stoll, Helv. Phys. Acta **27** (1954), 395.
[3] W. W. Titterton, T. A. Brinkley, Proc. Phys. Soc. **66A** (1953), 579.
[4] P. Stoll, M. Wächter, Nuovo Cimento **10** (1953), 374.
[5] H. Nabholz, P. Stoll, H. Wäffler, Helv. Phys. Acta **25** (1952), 701.
[6] E. Guth, C. J. Mullin, Phys. Rev. **76** (1949), 234.
[7] J. A. Wheeler, Phys. Rev. **52** (1937), 1083.

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EXPERIMENTAL PHYSICS

An Electron-Photon Shower of Very High Energy Registered in Nuclear Emulsions

by

A. JURAK, M. MIĘSOWICZ, O. STANISZ and W. WOLTER

Presented by H. NIEWODNICZAŃSKI on June 3, 1955

Electron-photon showers, with energies $\sim 10^{10}$ eV, observed in photographic emulsions were first described by Hooper et al. [1] and later by others (see, e. g. Gottstein [2]). Soft cascades have also been observed in connection with high energy interactions as a consequence of π° decay [3], [4], [5]. Quite recently Schein et al. [6] and Debenedetti et al. [7] described electron-photon showers interpreted by them as showers generated by several independent photons.

In a stack consisting of 20 Ilford G5-600 μ stripped emulsions, which during the Sardinian Expedition of July 13, 1953, were exposed at a height of about 20,000 m. we noted an event in which the picture consisted of a shower of very energetic pairs of charged particles, without any other tracks of ionising particles in the neighbourhood. The point of production of the first pair was inside the emulsion. The shower then went through 18 emulsions. The total length of the shower observable in the stack was about 7.5 cm. All the origins of the pairs are enclosed in a cone with a half angle $\leqslant 0.001$ radians. A closer analysis of all the tracks showed that out of the 13 pairs observed, only two pairs, viz. Nos. 7 and 11, have origins which can be clearly separated from the other tracks. All the other pairs have origins which are indistinguishable (within the limits of 0.5 μ) from the other tracks. These are "apparent tridents", i. e., pairs generated by highly collimated photons converted indistinguishably close to the parent path of high energy electron, or pairs generated directly by electrons, "true tridents" (See Block and King [8], and also Koshiba and Kaplon [5]). So far, we have investigated the points of origin of the first 13 pairs over a length of 45,000 μ.

The energies of the pairs were roughly estimated from the angles between the particle tracks; for this purpose we used Stearns' formula [9], assuming that particles were electrons taking equal energies from the

photon. In evaluating the energies of pairs, multiple scattering was not taken into account except in the case of the first pair. On account of this, the values for the energies of the pairs in Table I have been underestimated. If, instead of Stearns' formula, we use that of Borsellino [11], which gives smaller angles for the same energy, a correction for scattering should be used, which gives values for energies not very different from those given in Table I.

TABLE I

Pair	Distance from the point of origin of the first pair (μ)	Minimum energy of the photon (eV)
1	0	2×10^{11}
2	9390	2.6×10^{9}
3	16390	2.3×10^{8}
4	17500	9×10^{9}
5	23830	4×10^{8}
6	27820	2×10^{10}
7	29990	2×10^{8}
8	30610	2.6×10^{9}
9	34890	2.8×10^{10}
10	38710	2.5×10^{8}
11	40880	7.5×10^{10}
12	42790	1.6×10^{10}
13	43540	1.8×10^{9}

In Table I are collected the data concerning the pairs which belong to the shower down to a depth of 45,000 μ. For greater depths the number of tracks is larger and there are difficulties in resolving the individual tracks. At a depth of 75,000 μ at the point where the shower emerges from the stack, we have about 100 tracks in a cylinder with a radius of 500 μ, though the great majority of tracks lie within quite a narrow cone.

We have tried to describe our event as an electron-photon cascade initiated by a single photon of high energy. We used, for this purpose, data from the Tables of Jánossy and Messel [10] taking into account ionisation losses in the second approximation of the cascade theory. For the radiation length in G5 emulsions we took the value of 3.1 cm.

A shower is considered as being the sum of two cascades, the primaries of which are the electrons of the first pair, assuming they have equal energies. We calculated the number of electrons that might be expected to have energies higher than the critical energy in the emulsion (20 MeV) for a depth of 45000 μ ($=1.45$ rad. length).

Figures are given in Table II for three intervals of energy. These figures are compared with the number of electrons from pairs which we

observed, taking into account radiation losses between the point of origin of the pair and the depth of observation. The figures in the 2-nd column of Table II were evaluated for the energy of the primary photon equal to 10^{11} eV. This value was taken in order to get the best agreement with the data for the two lowest energy intervals and also agreement with the value of the energy of that first pair given in Table I.

TABLE II

Energy interval eV	Number of electrons	
	calculated from cascade theory	observed
$>2\times10^9$	5	12
$2\times10^8-2\times10^9$	7	6
$2\times10^7-2\times10^8$	11	8

We observe that the number of high-energy electrons clearly exceeds the number predicted by the theory. This discrepancy cannot be avoided when we assume a higher energy for the first pair. In this case the discrepancy between the numbers of low and high-energy electrons is a large one. It is possible that the very large fluctuations which occur in the first stage of the development of a cascade may explain this excess of high-energy pairs. There are also some other possible explanations for this discrepancy.

It is possible to assume that we have here several unconnected photons in the cascade process, i. e., we have here a phenomenon similar in type to the photon cascade observed by Schein at al. [6] and by Debenedetti et al. [7]. This event could be explained with the help of about 4 independent photons converted in the lower part of the investigated region of the shower. But in this case we should have to assume an extremely strong collimation of the photons, which would rather suggest that we have here cascade generation.

It seems possible that among our 10 apparent tridents we have some true tridents. This assumption could give us a suitable picture of what we would observe if the mean free path for trident production by electrons having an energy of 10—100 BeV were about one radiation length according to the value given in a recent paper by Koshiba and Kaplon [5].

A full analysis of this case is now being worked out.

The authors express their gratitude to Professor M. Danysz for many very helpful discussions and to Profsesor C. F. Powell for the stack of emulsions from the Sardinian Expedition.

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REFERENCES

[1] J. E. Hooper, D. T. King, A. H. Morrish, Canad. J. Phys. **29** (1951), 545.
[2] K. Gottstein, *Kosmische Strahlung*, W. Heisenberg, Springer 1953, page 358.
[3] M. Kaplon, B. Peters, D. M. Ritson, Phys. Rev. **85** (1952), 900.
[4] J. M. Mulvey, Proc. Roy. Soc. A **221** (1954), 367.
[5] M. Koshiba, M. F. Kaplon, Phys. Rev. **97** (1955), 193.
[6] M. Schein, D. M. Haskin, R. G. Glasser, Phys. Rev. **95** (1954), 855.
[7] A. Debenedetti, C. M. Garelli, L. Tallone, M. Vigone, G. Wathagin, Nuovo Cimento, **12** (1954), 954.
[8] M. M. Block, D. T. King, Phys. Rev. **95** (1954), 171.
[9] M. Stearns, Phys. Rev. **76** (1949), 836.
[10] L. Jánossy, H. Messel, Proc. Roy. Irish Ac. **54** (1951), 217.
[11] A. Borsellino, Phys. Rev. **89** (1953), 1023.

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EXPERIMENTAL PHYSICS

Some Notes on Low-Energy Gamma-Radiation at Great Depths

by

M. MIĘSOWICZ, L. JURKIEWICZ and J. M. MASSALSKI

Presented by H. NIEWODNICZAŃSKI on June 3, 1955

M. Ageno, G. Cortellessa and R. Querzoli [1] describe measurements with a scintillation counter performed in a laboratory at sea level. These measurements were concerned with photon radiation of rather high intensity and of very low energy, the spectrum having a distinct peak at about 100 keV. They consider this radiation to be due to cosmic radiation, and suggest the possibility that the low-energy γ-radiation observed by us in our measurements at great depths may also be of the same type. The purpose of this paper is to discuss the problem of low-energy photon-radiation at great depths in connection with the suggestion of Ageno et al. (l. c.).

The phenomenon which we have investigated at great depths underground was discovered by Barnóthy and Forró [2], [3], [4]. They found that at depth of 1000 m. w. e. there were more double than triple coincidences registred in the G. M.-counter-telescope (in the same solid angle). They also found that the radiation causing this excess of double coincidences was isotropic. They tried to connect this radiation with the cosmic radiation penetrating to that depth.

We confirmed these observations in our measurements at 540 and 660 m. w. e. [5], [6] and, after estimating the efficiency of the telescope for registering coincidences due to low-ionizing radiation and measuring its absorption in lead, we suggested that the effect mentioned above might be due to photons with energies of about 1 MeV, deriving from the radioactive contaminations of the surroundings.

This suggestion was proved by two of us [7] in the following way. It was found that the intensity of this low-ionizing radiation was entirely independent of the intensity of cosmic radiation, which is a known function of the depth. The intensity of this low-ionizing radiation was found to be proportional to the intensity of the local γ-radiation (see Table I),

which was separately registered by means of a single G. M.-counter. The intensity of the local γ-radiation, on the other hand, is defined by the chemical composition of the geological layers at the place of measurement. Because of the differences in the geological layers at different places, the intensity of the local γ-radiation at a given depth in the mine varies within wide limits. We found at the same depth of 313 m. w. e. two places, 15 m. apart, which differed both in their geological aspect and in their local γ-ray intensity. One of these two places was surrounded by silt and the other by rock-salt. Different values were found in these two places for the intensity of low-ionizing radiation, giving an excess of double coincidences over triple ones. Table I shows the results of our measurements at different depths underground.

TABLE I

Depth m. w. e.	Surroundings	Triple coincidences T/h	Double coincidences D/h	$A=D-T$ per hour	Number of pulses above the background N/min.	$A/N \times 10^2$	A/T
1	2	3	4	5	6	7	8
145	silt	42.2 ± 0.5	45.3 ± 0.5	3.1 ± 0.15	301 ± 5.5	1.03	0.073
220	rock-salt	16.3 ± 0.5	17.1 ± 0.5	0.8 ± 0.1	83 ± 5.5	0.96	0.049
313	„ „	8.5 ± 0.4	10.2 ± 0.4	1.7 ± 0.2	153 ± 6	1.11	0.20
313	silt	8.2 ± 0.4	14.3 ± 0.5	6.1 ± 0.3	543 ± 4.5	1.12	0.74
415	rock-salt	3.78 ± 0.3	4.65 ± 0.2	0.87 ± 0.1	99 ± 3	0.88	0.23
545	„ „	1.94 ± 0.07	2.70 ± 0.09	0.76 ± 0.05	82 ± 3.6	0.93	0.39
660	„ „	1.38 ± 0.06	1.91 ± 0.07	0.53 ± 0.04	51 ± 3	1.04	0.38

The intensity of local γ-radiation is proportional to the number N given in column 6 of Table I, N being the number of pulses (per minute) produced in a single counter by the γ-radiation of the environment. N was obtained by subtracting the rate of pulses due to its background and the rate of pulses due to the ionizing component of the cosmic radiation from the rate of pulses observed in the counter. It can be seen from Table I, column 7, that there is a proportionality between the rate of coincidences caused by low-ionizing radiation and the rate of pulses due to local γ-radiation, but it is not possible to find any proportionality between the rate of coincidences caused by low-ionizing radiation and the rate of coincidences due to cosmic rays (see column 8 of Table I).

We suggested the following mechanism for registering the double coincidences caused in our telescope by this radiation. The γ-photon, on going through the first counter, discharges it by a Compton electron,

and the scattered photon discharges the second counter in the usual way. This mechanism was investigated by Gierula [8] and by Barnóthy and Forró [9]. In Gierula's experiments, which were carried out in our laboratory, a beam of collimated γ-rays fell on one G. M.-counter and the scattered radiation on a second one. The coincidences of pulses from these two counters were recorded. Gierula investigated the angular dependence of these Compton-coincidences. Integrating the angular distribution of this effect for an isotropic γ-radiation, he obtained a result comparable to that which we observed in the mine. In this way Gierula has demonstrated that there exists an agreement between the efficiency of the telescope registering the double coincidences in the mine and the efficiency of a similar telescope registering the Compton-coincidences due to the γ-radiation emitted by natural radioactive substances.

The Compton-coincidences caused by local γ-radiation should be looked upon as a very rare phenomenon which is difficult to detect with a G. M.-counter-telescope in a laboratory at ground level, because of the high background of coincidences due to cosmic rays, mainly accidental coincidences. The occurrence of these coincidences deep underground is explained by the fact that the rate of accidental coincidences decreases in proportion to the square of the rate of pulses in a single counter, whereas the rate of Compton-coincidences decreases in proportion only to the first power of the latter.

It is also interesting to compare the intensity of the low-energy γ-ray photons recorded in our underground experiments with that of of the vertical ionizing cosmic radiation. Taking the efficiency of our counter telescope for registering γ-ray photons of an energy $\sim$1 MeV as equal to about 10^{-5}, we obtain, for a depth of 660 m. w. e., about 4.10^4 photons per one ionizing cosmic ray particle (in the same solid angle). For photons of energies of about 100 keV this number should be still higher because of the lower efficiency value of telescope for registering them. We can compare this figure with that given by Ageno et al. —100 photons per one ionizing cosmic-ray particle.

All these arguments support our former assumption that the photon radiation investigated by us at great depths must be considered as a γ-radiation of local origin. This conclusion has also been confirmed by Bollinger [10] and by Randall et al. [11].

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REFERENCES

[1] M. Ageno, C. Cortellesa and R. Querzoli, Il Nuovo Cim., **12** (1955), 453.
[2] J. Barnóthy and M. Forró, Phys. Rev., **55** (1939), 870.
[3] — *Symposium on cosmic rays*, Cracow, Oct. 1947.

[4] — Phys. Rev., **74** (1948), 1300.

[5] M. Mięsowicz, L. Jurkiewicz and J. M. Massalski, Acta Phys. Pol., **10** (1950), 69.

[6] — Phys. Rev., **77** (1950), 380.

[7] M. Mięsowicz and J. M. Massalski, Acta Phys. Pol., **10** (1950), 274.

[8] J. Gierula, Acta Phys. Pol., **11** (1950), 36.

[9] J. Barnóthy and M. Forró, Midwest Cosmic Ray Group Meeting, Ann Arbor, 1950.

[10] L. M. Bollinger, Phys. Rev., **79** (1950), 207.

[11] C. A. Randall, N. Sherman and W. R. Hazen, Phys. Rev., **79** (1950), 905.

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CHEMISTRY

Separation of Nitroparaffins from their Mixtures and Identification of Mononitrocompounds

by

T. ŚLEBODZIŃSKI and L. MAKARUK

Communicated by T. URBAŃSKI at the meeting of December 13, 1955

The nitration of paraffins with nitric acid or nitrogen dioxide in the gaseous phase gives a number of nitration and oxidation products. The research carried out by T. Urbański et al. [1], as well as that of H. B. Hass and his collaborators [2], [3], has already shown that even during the nitration of pure, simple members of the paraffin series, such as propane, *n*-and isobutane, *n*-and isopentane etc., besides nitroparaffins, which are the main products of reaction, oxidation products — aldehydes, ketones and acids — are obtained, depending on the reaction conditions and the ratios of the substrates used. The separation and identification of the mononitroparaffins, after the preliminary and comparatively easy separation of the oxidation products and the partial separation of the dinitroderivatives which, according to T. Urbański et al. [1], are also formed during nitration with excess of nitrogen dioxide, can only be carried out with difficulty and a low degree of accuracy.

The methods proposed by some authors (Hass et al. [2], [3]) do not seem easy to carry out, e. g. identification by means of a comparison of the melting points of amine hydrochloride mixtures, obtained from suitable nitroparaffins, with the freezing point curves of standard mixtures of the same hydrochlorides.

In our present investigations into nitration of *n*-hexane with nitrogen dioxide, carried out within a wide range of hydrocarbon/NO_2 ratios [4], we used small quantities of *n*-hexane for nitration, and obtained relatively small quantities of lower mononitroparaffins in individual experiments. Such small quantities of the mixtures could not be separated with a satisfactory degree of purity by distillation on Weston's column. That is why we were anxious to discover a more suitable method for the separation and identification of nitroparaffins from the fractions obtained on Weston's column.

Of the many experiments carried out in this direction, the most encouraging seemed to be the coupling of nitroparaffins with diazonium compounds. This reaction was discovered by V. Meyer [5] and improved upon by E. Bamberger [6]. Primary and secondary nitroparaffins undergo condensation, according to the following reactions:

$$(RCH{=}NO_2)^{(-)}Na^{(+)} + C_6H_5\overset{+}{N}_2\overset{-}{Cl} \rightarrow \underset{\text{I}}{C_6H_5{-}N{=}\overset{|}{\underset{NO_2}{C}}HR} \rightarrow$$

$$\rightarrow \underset{\text{II}}{C_6H_5NHN{=}\overset{|}{\underset{NO_2}{C}}R}$$

and

$$(R_1R_2C{=}NO_2)^{(-)}Na^{(+)} + C_6H_5N_2Cl \rightarrow \underset{\text{III}}{C_6H_5{-}N{=}N{-}\overset{R_1}{\overset{|}{\underset{R_2}{C}}}NO_2}$$

These reactions were studied later by Dermer and Hutcheson [7]. They suppose that these condensations might be of use for the identification of nitroalkanes. This opinion seems to be right, since, in contradiction to other methods of nitroparaffin identification, the coupling reactions proceed with a high yield (85—90%), condensation can be readily carried out, and the products obtained are comparatively pure and crystallise easily. Table I gives details concerning some derivatives:

TABLE I

Nitroparaffin	Coupled with diazonium salt from:	Raw product yield data		Yield after crystallisation (our data)	Melting point °C.
		ours	other authors'		
Nitromethane *)	aniline	a) 39%	—	25%	a) 92
		b) 35%	—	29%	b) 153
Nitromethane [7]	*p*-nitroaniline		—		159
Nitroethane [6], [7]	aniline	85.5%	theor. [6]	68%	139—142
Nitroethane [6], [7]	*p*-nitroaniline		—		157
1-Nitropropane [6], [7]	aniline	90%	87% [6]	67%	98—101
1-Nitropropane [7]	*p*-nitroaniline		—		139—140
2-Nitropropane [7]	aniline		—		oil
2-Nitropropane [7]	*p*-nitroaniline	85%	—	80%	105—107

*) Nitromethane, depending on the conditions of reaction, may react: a) with 1 molecule of benzenediazonium salt [8], [9] or b) with 2 molecules, yielding N, N'-diphenyl — C — nitroformazan [9].

nitromethane, nitroethane, and 1- and 2- nitropropanes, according to data from the literature as well as our own.

Data concerning new compounds, not yet described in the literature, are given in Table II.

TABLE II

Nitroalkane	Coupling with diazonium salt from:	Obtained phenyl or *p*-nitrophenyl hydrazone of	Melting point	N content in percent	
				calculated	found
1-nitrobutane	aniline	1-nitrobutanal	66– 67°C.	20.3	20.6
1-nitrohexane	aniline	1-nitrohexanal	57– 60°C.	18.2	18.0
1-nitrobutane	*p*-nitroaniline	1-nitrobutanal	120–121°C.	22.2	21.8
1-nitropentane	*p*-nitroaniline	1-nitropentanal	118.5–119°C.	21.1	21.7
1-nitrohexane	*p*-nitroaniline	1-nitrohexanal	116.5–118°C.	20.0	19.5

As can be clearly seen, both from data collected from the literature and from our own, primary nitroparaffins, when condensed with diazonium aniline, give phenylhydrazones of nitroaldehydes (II) which are solid substances, whereas secondary mononitroalkanes in these same conditions give liquid benzene-azonitroalkyls (III). Hence, primary and secondary mononitroparaffins may be separated in this very way. In order to ascertain, whether it was possible to apply the above reaction for the separation of such nitroparaffins, a number of mixtures were prepared and experimented upon; e. g., from a mixture of equimolar quantities of primary and secondary nitropropane, by means of coupling with benzenediazonium acetate and separation of the precipitated crystalline precipitate, there was obtained raw phenylhydrazone of 1-nitropropanal with a theoretical yield of 80% (Table III), i. e. with a yield almost

TABLE III

No.	Mixture of primary and secondary nitroparaffins	Coupled with diazonium salt from:	Raw phenylhydrazone of 1-nitropropanal		Purified product	
			yield in %	melting point	yield in %	melting point
1)	50% 1-nitropropane 50% 2-nitropropane	aniline	82	91– 96°C	70	98–101°C
2)	50% 1-nitropropane 50% 2-nitropropane	aniline	79	101–102°C	71	101–102°C

the same as that attained by Bamberger when he condensed pure 1-nitropropane.

Similar results for the separation of the conjugation products of primary and secondary nitroparaffins with benzenediazonium salts may also be obtained by availing oneself of the ability of phenylhydrazones of nitroaldehydes to form sodium salts, in contradistinction to azocompounds, which are the products of secondary nitroparaffin coupling, and which do not possess this property. A mixture of the coupling products of primary and secondary nitropropane with benzenediazonium acetate, after being dissolved in ether, was shaken with 2.0% NaOH.

From the separated water solution, after acidification with acetic acid, pure phenylhydrazone of 1-nitropropanal was obtained with a yield of about 80 per cent.

Mixture No.2 was separated by the transformation of phenylhydrazone of 1-nitropropanal into water-soluble sodium salt.

The obtained phenylhydrazones of 1-nitroaldehydes, however, are not stable compounds. When kept in a closed vessel, they decompose by themselves. This fact was noted earlier by Bamberger [6]. We also observed decomposition in some cases, and even just after a few days. But well-purified coupling products kept in the open air did not show any visible changes (for several months).

In order to transform the products of coupling of primary nitroparaffins with benzenediazonium salts into more stable substances, we availed ourselves of Bamberger's [6] hydrolysis of phenylhydrazones of 1-nitroaldehydes. By heating for some minutes with surplus 0.3 *n* NaOH, stable phenylhydrazides of fatty acids were obtained, formed according to the equation:

$$C_5H_6NHN{=}\underset{\underset{NO_2}{|}}{C}H_2R + NaOH \rightarrow C_6H_5NHNHCOCH_2R + NaNO_2$$

As is well known, these compounds are identical with the products of direct condensation of phenylhydrazine with the corresponding fatty acids:

$$C_6H_5NHNH_2 + HOOCR \rightarrow C_6H_5NHNHOCR + H_2O$$

The above method was used for investigating mixtures of mononitroparaffins obtained while nitrating *n*-hexane with nitrogen dioxide in the gaseous phase. In this way we succeeded in separating and identifying primary mononitroparaffins, which formed apparently uniform fractions isolated by means of Weston's column.

Detailed results of these investigations will be published elsewhere [10].

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REFERENCES

[1] T. Urbański, M. Słoń, Roczniki Chemii **16** (1936), 466; **17** (1937) 161. Compt. rend. **203** (1936), 620; **204** (1937), 870.

[2] Hass, Patterson, Ind. Eng. Chem. **31** (1939), 648.

[3] Seigle, Hass, Ind. Eng. Chem. **30** (1938), 67.

[4] T. Urbański, T. Ślebodziński, A. Łukasiewicz, Roczniki Chemii (in press).

[5] V. Meyer, G. Ambühl, Ber. **8** (1875), 751.

[6] E. Bamberger, Ber. **31** (1899), 2626.

[7] Dermer, Hutcheson, Proc. Oklahoma Acad. Sci. **23**, 60; Chem. Abstra. **38** (1944), 2006.

[8] E. Ch. S. Jones, J. Kenner, J. Chem. Soc. (1930), 925.

[9] E. Bamberger, Ber. **27** (1894), 155.

[10] T. Ślebodziński, L. Makaruk, Roczniki Chemii (in press).

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CHEMISTRY

A Method for Determining the Composition of Quaternary Azeotropes and the Position of Heteroazeotropic Lines

by

K. ZIĘBORAK and A. GALSKA

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of May 13, 1955

1. Introductory remarks.

A method for determining the composition of quaternary azeotropes was suggested recently by Świętosławski [1]. This paper resulted from Zięborak's [2] observation that some paraffins such as isooctane, *n*-heptane, and cyclohexane, form quaternary azeotropes with benzene, ethanol and water. In this paper another method for examining the composition of quaternary heteroazeotropes is presented. This method may be applied in all cases in which the determination of the concentration ratio of two components, e. g., $B:C$, for an azeotrope obtained by fractional distillation is an easy operation. First, it is necessary to find the position of the heteroazeotropic line on the models shown in Figs. 2 and 3. Once that is done, the composition of the azeotrope under examination may be found by determining the composition of only one of the components in the azeotrope obtained by careful fractional distillation.

2. Preparation of substance.

In our investigation the system composed of benzene (B) — cyclohexane (C) — ethanol (E) — water (W) was chosen. Both benzene and cylohexane were thoroughly purified by rectification of the chemically pure reagents. The benzene sample was found to be of the fifth degree of purity, according to the ebulliometric scale [3]. In fact the difference between the boiling and the condensation temperatures δt was equal to 0.002°C. Cyclohexane of the fourth degree of purity was obtained (σt=0.009°C).

3. Methods of investigation.

Two Świętosławski ebulliometers were used, one differential, the other one-stage for controlling pressure changes. Measurements were taken in a strictly comparative way as described in Świętosławki's monograph [3].

4. Ternary system (C,E,W).

First of all the position of the heteroazeotropic line in the ternary system (C, E, W) was determined. Mixtures of cyclohexane and ethanol, their composition being indicated in the concentration triangle by points D', D'' and D''' (Fig. 1) were successively introduced into a differential ebulliometer. Next, small portions of water were added, the boiling and condensation temperatures of the mixtures being observed after each addition. In three successive series of measurements A_1, A_2, A_3 (upper part of Fig. 1) curves were obtained which showed abrupt minima of temperatures t_b and of condensation temperatures t_c. These minima corresponded to the crossing point of the heteroazeotropic line. Thus, by projecting these minima on to Gibbs' concentration triangle (Fig. 1) the position of the heteroazeotropic line FGI of the ternary (C, E, W) system was graphically represented.

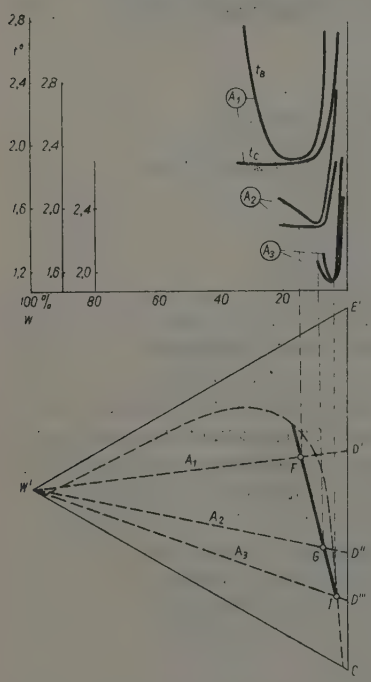
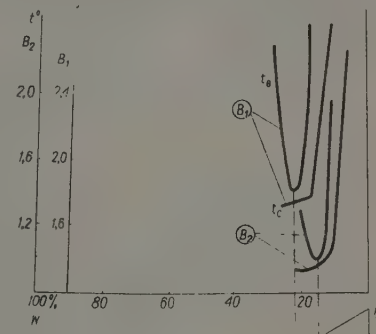


Fig. 1. Determination of the position of the heteroazeotropic line FGI in the system: cyclohexane (C)-ethanol (E)-water (W). The upper part shows the changes in the boiling temperature t_b and in the condensation temperature t_c caused by the change in the water content of the mixture.

The boiling temperature azeotrope of (C, E, W) was found to be equal to 62.60°C±0.05°C. The mixture represented graphically by point I was rectified, the cyclohexane content was determined in the distillate, and the contents of the other components were computed on the basis of the diagram (Fig. 1). The composition of the azeotrope under examination, expressed in weight per cent, was as follows: 75.5%(C), 19.7%(E), 4.8%(W).

5. Quaternary system (*C*,*B*,*E*,*W*).

The geometrical representation of any property of a quaternary system may be realised in different ways, one of these ways being by the methods proposed by Fiodorov, Boecke, Radischchev [4]. When it is necessary to define the composition of a quaternary mixture, then a tetrahedron is mostly used. If, however, some properties of the system are to be represented, projections onto the tetrahedron are used. While examining the system under consideration, it was observed that among the four corresponding ternary systems:



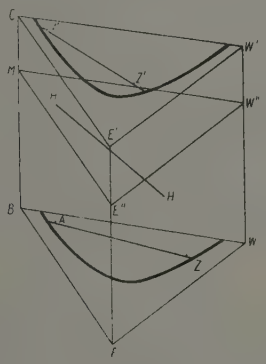


Fig. 2. A regular triangular prism; *B* — benzene, *E* — ethanol, *W* — water, *C* — cyclohexane; *AZ* and *AZ'* the heteroazeotropic lines in the (*B*, *E*, *W*) and (*C*, *E*, *W*) azeotropes; *HH'* the heteroazeotropic line of the quaternary azeotrope (*B*, *C*, *E*, *W*).

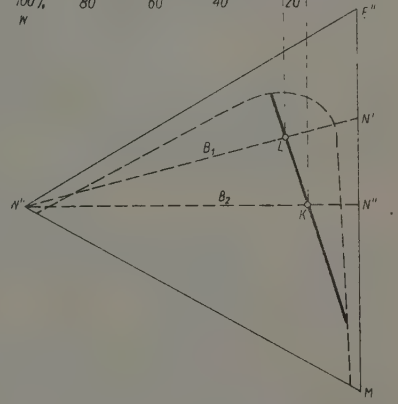


Fig. 3. Determination of the position of the heteroazeotropic line in the *ME''W''* section for which the ratio *BM*:*MC* = = const. = 2.7; t_B and t_C — boiling and condensation temperature isobars measured by a Świętosławski ebulliometer.

(*B*, *E*, *W*); (*C*, *E*, *W*); (*B*, *C*, *E*); (*B*, *C*, *W*) two are very similar to each other, namely the (*B*, *E*, *W*) system investigated by Barbaudy [5] and the (*C*, *E*, *W*) one just described. In both these systems ethanol plays the rôle of a homogeniser because both benzene and cyclohexane are practically insoluble in water. Moreover, the azeotropes (*C*, *E*, *W*) and (*B*, *E*, *W*) are characterised by lower boiling temperatures than the two others. This specificity of the (*C*,*B*,*E*,*W*) system leads us to use a regular triangular prism for representing the composition of quaternary mixtures (Fig. 2).

In a further continuation of the experimental work, the position of the heteroazeotropic line lying in the *MEW* section of the regular

prism was determined (Fig. 2). This section corresponds to quaternary mixtures characterised by a constant concentration ratio of cyclohexane and benzene. As mentioned above, this ratio may be determined quite easily (2). For the quaternary azeotrope it was as follows; $BM:CH=2.7:1$. The results of our measurements are represented on the concentration triangle (Fig. 3); the mixture of cyclohexane and benzene, being constant, may be considered as one component. The position of the "heteroazeotropic line" in a quaternary system is medial to its position in the corresponding (B, E, W) and (C, E, W) systems, as shown in (Fig. 4).

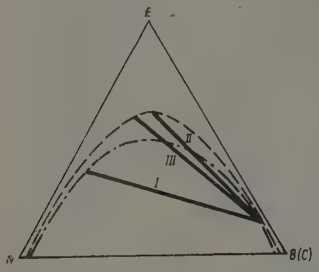


Fig. 4. Projections of three heteroazeotropic lines *I*, *II*, *III* on the prism plane (Fig. 2) corresponding to the (B,E,W), (C,E,W), (B,C,E,W) systems

In order to determine more precisely the inclination of the heteroazeotropic line *III* in a quaternary system in relation to the two others (*I* and *II*), two series of measurements were carried out, in which the boiling and the condensation temperatures were determined for four-componemt mixtures formed by miving three-component mixtures, represented on the model (Fig. 2) by points. *A* and *Z* on one side and *A'* and *Z'* on the other. In both cases the minimum boiling temperatures were found, and these enabled us to determine more precisely the position of the heteroazeotropic line *HH'*.

Finally, the quaternary azeotrope was prepared by careful rectification on a column provided with a special head for the distillation of heteroazeotropes. The weight per cent composition of this azeotrope was determined and was as follows: 54.3%(*C*), 19.2%(*E*), 6.1%(*W*), 20.4%(*B*).

Summary

1. The composition of a quaternary heteroazeotrope formed by cyclohexane (*C*) benzene (*B*), ethanol (*E*), and water (*W*) was determined. Its composition expressed in weight per cent is as follows: 54.3% C; 20.4% *B*; 19.2% *E*; 6.1% *W*, and its boiling temperature is 62.14°C. (± 0.05°C). These data differ slightly from those given earlier [2].

2. A method was described for the ebulliometric determination of the position of the heteroazeotropic line in a quaternary system. This method is based on determination of the concentration ratio of two of the components, those that are most closely related as regards their physicochemical properties. In the case under consideration these were benzene and cyclohexane.

3. A model of a regular triangular prism was used for representing a four-component system in which two substances are present, not mixing with the third one. Such a method of system-representation facilitates the construction both of tie- and heteroazeotropic lines.

4. The composition of the ternary heteroazeotrope (*CEW*) was determined. It contains in weight per cent: 75.5% C; 19.7% *E*; 4.8% *W*; and is characterised by a boiling temperature of 62.60°C. The heteroazeotropic line forms the smallest acute angle with side *EC* (Fig. 4).

We express our thanks to Professor W. Świętosławski for his valuable advice.

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REFERENCES

[1] W. Świętosławski, A. Galska, Bull. Acad. Polon. Sci., Cl.III, **2** (1954), 497.

[2] K. Zięborak, Prace Głów. Inst. Chem. Przem. **1** (1952), 1; Bull. Acad. Polon. Sci., A (1950), 92.

[3] W. Świętosławski, *Ebulliometric measurements*, Reinhold Publ. Corp. New York, 1945.

[4] W. P. Radishchev, Izv. Sektora Fiziko-Chim. Analiza (U.S.S.R.) **15** (1947), 5.

[5] J. Barbaudy, Compt. Rend. **181** (1925), 1924.

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CHEMISTRY

On the Formation of Derivatives of 5-Nitrotetrahydro-1,3-Oxazine Substituted in Position 2

by

H. PIOTROWSKA and T. URBAŃSKI

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Previous papers [1] on the formation of 5-nitrotetrahydro-1,3-oxazine derivatives have dealt with a method consisting in the cyclisation of derivatives of 3-aminoalcohols with formaldehyde. It has now been found that other aldehydes, both aliphatic and aromatic, can be used to yield 5-nitrotetrahydro-1,3-oxazine derivatives substituted in position 2.

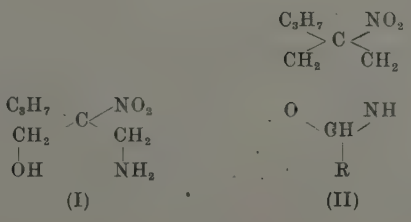
2-nitro-2-hydromethyl-pentylamine (I) has now been subjected to cyclisation by means of aldehydes: acetic, propionic, *n*-butyric, benzoic, *p*-chloro-, *o*-and *p*-nitro-, *p*-hydroxybenzoic.

The starting product (I) was prepared from 1-nitrobutane, formaldehyde and ammonia, as previously described by the authors [2].

The reaction of (I) with formaldehyde to yield (II) ($R=H$) occurred readily and with an excellent yield, as a result of warming (I) with aqueous formaldehyde. When the other aldehydes were used, it was necessary to carry out the reaction in an anhydrous medium: by boiling either in ethanolic or in benzene solution. In the latter case it was possible to distill off the reaction water, in the form of azeotrope with benzene. Both methods gave approximately the same yield of (II).

When aliphatic aldehydes were used, the yield of (II) was very small and a considerable quantity of dark-coloured resinous by-products were formed.

Aromatic aldehydes reacted with (I) more readily, the yield being 70-80%. A particularly good yield was obtained with *p*-nitrobenzaldehyde.



(I) (II)

The following products (II) were thus obtained:

No.	*R*	Yield %	m. p.			
			Free base	Hydrochloride	Picrate	N-nitrozo derivative
1	H	80	liquid	190–192°	163–164°	liquid
2	CH_3	5	liquid	178–180°	145–146°	liquid
3	C_2H_5	5	liquid	182–184°	137–138°	liquid
4	*n*-C_3H_7	7	liquid	174–176°	139–140°	liquid
5	C_6H_5	60	liquid	180–182°	–	liquid
6	*p*-ClC_6H_4	75	56– 57°	170–172°	–	71– 72°
7	*o*-$NO_2C_6H_4$	70	93– 94°	178–180°	–	99–100°
8	*p*-$NO_2C_6H_4$	90	101–102°	174–176°	–	109–110°
9	*p*-HOC_6H_4	65	111–112°	184–186°	–	–

All the hydrochlorides of (II), when warmed with hydrochloric acid, were subjected to hydrolysis with cleavage of aldehyde and product (I) resulted.

The reaction occurred particularly readily when hydrochloric acid, diluted with ethanol to c. 1.5% HCl, was used. The aldehydes freed during this reaction were identified as 2,4-dinitro-phenylhydrazones.

Some hydrochlorides showed insufficient stability. E. g. the hydrochloride of No. 5, i. e., of 2-phenyl-5-nitro-5-*n*-propyl-tetrahydro-1,3-oxazine, when kept at room temperature for a few hours underwent considerable decomposition. In some instances, crystallisation of hydrochlorides (II) produced a lowering of the m. p.

Free bases show much greater stability. Their m. p. remains unchanged when stored for several weeks.

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REFERENCES

[1] E. L. Hirst, J. K. N. Jones, S. Minahan, F. W. Ochyński, A. T. Thomas, T. Urbański, J. Chem. Soc. (1947), 924; T. Urbański, D. Gürne, Roczniki Chem. **28** (1954), 175.

[2] T. Urbański, H. Piotrowska, Roczniki Chem. **29** (1955), 379.

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CHEMISTRY

Thermodynamic Properties of the Silver-Zinc System and the Related β-AgMg Phase

by

W. TRZEBIATOWSKI and J. TERPIŁOWSKI

Communicated by W. TRZEBIATOWSKI at the meeting of May 16, 1955

The electromotive forces of the reversible galvanic cell

$$Zn_{liq}|(0.583\ LiCl+0.417\ KCl)+0.05\ ZnCl_2|Ag_xZn_{1-x}$$

were measured, using 60 silver alloys, containing 284—824 at $-{}^0/_{00}$ Zn, which were prepared from the purest components. The alloys were annealed for suitable times (120—300^h) at temperatures between 500-550°C. The cells, in the form of evacuated quartz tubes, were placed in the copper block of an electric furnace. The temperature of the latter was kept constant, within 3°, at between 428—600°. A good constancy of 0.1 mV and reproducibility of e. m. f. were attained after 3-33 hours. The e. m. f. was measured by a 5-decade potentiometer equipped with a sensitive mirror galvanometer.

The e. m. f. at 500° ($E_{500°}$) and the temperature coefficients (dE/dT) of these cells are given in Table I. The constant values of e. m. f. relate to the two-phase regions $\alpha+\beta$, $\beta+\gamma$, $\gamma+\varepsilon$ in accordance with the phase diagram of the Ag-Zn system [1]. The temperature coefficients observed within the β- and ε- phases proved that, in accordance with Oelander's [2] theoretical considerations, these phases represent, at the compositions AgZn and $AgZn_3$ also, disordered types of structure. The narrow existence range of the γ-phase renders such conclusions impossible. From X-ray analysis it was deduced [3] that the β-phase is disordered, but other authors [1], [4] have concluded that a certain degree of order exists. The disordered distribution of atoms in the ε-phase is in agreement not only with the results of X-ray analysis [1], [5], but also with those of other thermodynamic investigations [6]. From the experimental results the changes in the partial free energies (ΔF^1_{Zn}) and the entropy (ΔS^1_{Zn})

for the $Zn_{liq} \rightarrow Zn_{solid\ alloy}$ process were calculated:

$$\overline{\Delta F^1_{Zn}} = -nFE \qquad S^1_{Zn} = nF\frac{dE}{dT}.$$

The changes in the partial enthalpy ($\overline{\Delta H^1_{Zn}}$) were calculated according to the equation: $\overline{\Delta H^1_{Zn}} = \overline{\Delta F^1_{Zn}} + T\Delta\overline{S^1_{Zn}}$.

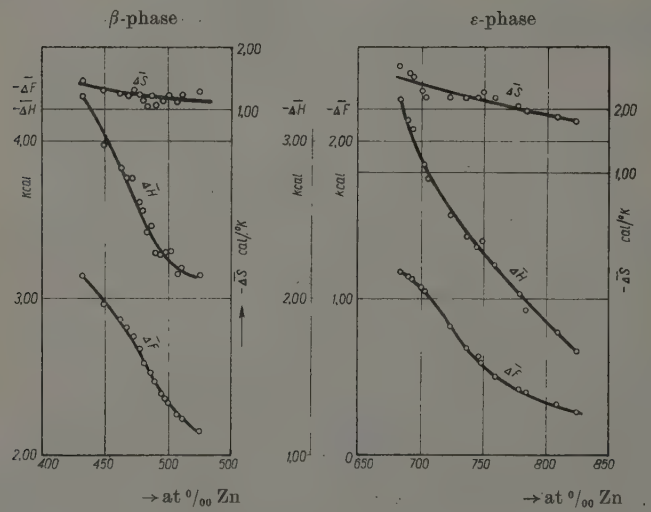

Fig. 1

The values of $\overline{\Delta F^1_{Zn}}$, $\overline{\Delta S^1_{Zn}}$ and $\overline{\Delta H^1_{Zn}}$ change gradually within the β- and ε-phase. Of course, within these phases the changes are small and this is significant for small interaction of components and typical for solid solutions or intermetallic phases composed of metals of neighbouring subgroups.

It is interesting to note that the zinc activities calculated from vapour pressure measurements are nearly the same as those obtained from the galvanic cell. C. E. Birchenall and C. H. Cheng [7] found with an alloy of 764.5 at-°/₀₀ Zn at 410° $-a_{Zn}=0.595$. From our experiments (Table I) and the formula $\overline{\Delta F^1_{Zn}} = RT \ln a_{Zn}$ one can calculate through interpolation for this composition at the fusing point of zinc ($T=693°$) $-a_{Zn}=$ $=0.621$.

The same kind of measurements were carried out with the β-phase of the silver-magnesium alloys at temperatures between 500–610°. The alloys were melted in vacuum from purest silver and magnesium (at least 99.95%) and annealed for 200 hours at 550°.

TABLE I

Experimental results and partial molar thermodynamic data of silver-zinc alloys

ΔT-°/₀₀ Zn	E_{500} mV	$\frac{dE}{dT}$ μV/1°	$-\overline{\Delta F^1_{Zn}}$ kcal	$-\overline{\Delta S^1_{Zn}}$ cal/1°	$-\overline{\Delta H^1_{Zn}}$ kcal	ΔT-°/₀₀ Zn	E_{500} mV	$\frac{dE}{dT}$ μV/1°	$\overline{\Delta F^1_{Zn}}$ kcal	$\overline{\Delta S^1_{Zn}}$ cal/1°	$\overline{\Delta H^1_{Zn}}$ kcal
α-phase						β+γ-phase					
284	113.3	−24	5.23	1.1	6.09	548	41.9	−63			
298	106.2	−22	4.90	1.0	5.69	560	42.2	−63			
313	100.9	−29	4.65	1.3	5.68	570	42.0	−63	1.94	2.9	4.19
322	97.9	−40	4.52	1.8	5.95	575	42.0	−63			
335	93.6	−49	4.32	2.3	6.07	593	42.0	−61			
349	89.8	−46	4.14	2.1	5.78	av. val:	42.0	−63			
352	88.1	−49	4.06	2.3	5.81						
357	86.8	−55	4.00	2.5	5.96	γ-phase					
360	85.7	−60	3.95	2.8	6.09	603	39.8	−68	1.84	3.1	4.27
369	82.6	−54	3.81	2.5	5.74	609	38.8	−75	1.79	3.5	4.47
						614	36.6	−83	1.69	3.9	4.65
α+β-phase						627	32.9	−67	1.52	3.1	3.91
386	70.9	+42									
390	71.0	+40				γ+ε-phase					
407	71.0	+41	3.28	−1.9	1.82	639	26.9	−54			
410	71.0	+40				649	27.1	−54			
413	71.0	+40				663	27.2	−56	1.25	2.5	3.21
av. val:	71.0	+41				667	26.9	−56			
						676	26.9	−56			
β-phase						av. val:	27.0	−55			
432	68.3	−32	3.15	1.5	4.29						
449	64.1	−28	2.96	1.3	3.96	ε-phase					
462	62.1	−27	2.87	1.3	3.83	685	25.4	−59	1.17	2.7	3.27
468	61.0	−27	2.81	1.3	3.77	690	24.8	−56	1.14	2.6	3.14
472	60.0	−28	2.77	1.3	3.77	693	24.3	−55	1.12	2.5	3.08
478	58.1	−26	2.68	1.2	3.61	702	23.3	−50	1.07	2.3	2.85
479	57.9	−25	2.67	1.2	3.56	705	23.0	−48	1.06	2.2	2.77
482	56.1	−23	2.59	1.1	3.41	725	18.0	−48	0.83	2.2	2.54
486	54.8	−26	2.53	1.2	3.46	738	14.7	−48	0.68	2.2	2.39
490	53.5	−23	2.47	1.1	3.29	747	13.5	−48	0.62	2.2	2.33
495	51.8	−25	2.39	1.2	3.28	749	12.8	−50	0.59	2.3	2.37
497	51.1	−26	2.36	1.2	3.29	759	10.8	−48	0.50	2.2	2.21
500	50.8	−27	2.34	1.3	3.30	779	9.0	−45	0.42	2.1	2.03
508	48.9	−25	2.26	1.2	3.15	784	8.6	−43	0.40	2.0	1.93
510	48.3	−27	2.23	1.3	3.19	809	7.1	−41	0.33	1.9	1.79
526	46.7	−28	2.15	1.3	3.15	824	5.9	−39	0.27	1.8	1.66

The following galvanic cell was built:

$$Mg_{sol}|(0.58\ LiCl+0.42\ KCl)+0.1\ MgCl_2|Ag_xMg_{1-x}$$

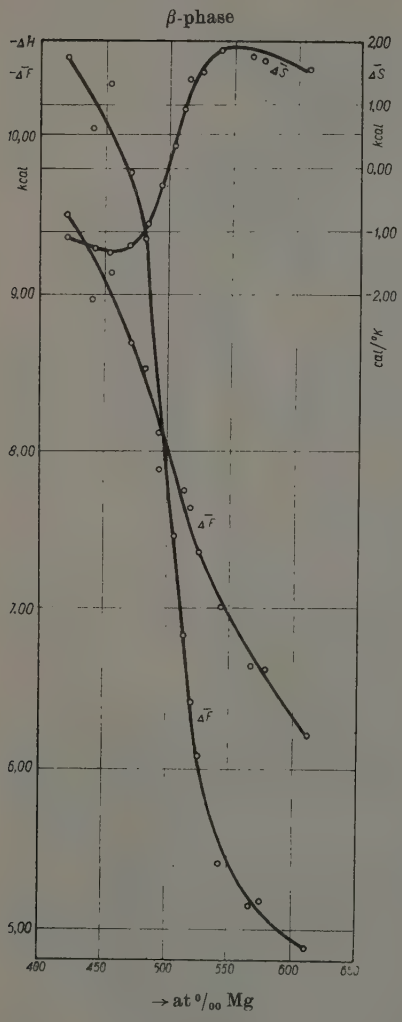

Fig. 2

The e. m. f. was measured in argon atmosphere giving a suitable constancy of 0.5 mV after 48-120 hours. The results are given in Table II, Fig. 2.

The β-phase AgMg has different thermodynamic properties as compared with the β-and ε-phase of the silver-zinc system. The changes in $\overline{\Delta F^s_{Mg}}$, $\overline{\Delta S^s_{Mg}}$ and $\overline{\Delta H^s_{Mg}}$ are more distinct as compared with the above-mentioned system and at the stechiometric composition a pronounced bending of the curves occurs. The changes in the partial molar entropy $\overline{\Delta S^s_{Mg}}$ are very characteristic and in accordance with those predicted for phases representing ordered distribution of atoms in the unit cell. From the slope of the curve a certain degree of "disorder" can be deduced, which may amount to 0.03 [2]. It is known from X-ray analysis that β-AgMg really offers ordered atomic distribution in the body-cubic cell [8], [9] and represents a well-known type of "daltonide" compound [10]. The typical "singular points" after Kurnakov on the curves of composition versus physical properties support this classification [11].

A further circumstance is characteristic for this type of "daltonide" compound. At the stechiometric composition the values of $\overline{\Delta S}$ is very small, therefore the partial molar enthalpy $\overline{\Delta H}$ and the partial free energy $\overline{\Delta F}$ are nearly equal. One can also observe such values from the experimental data given by Oelander [12] on the gold-cadmium β-phase, also a typical "daltonide" phase.

TABLE II

Experimental results and partial molar thermodynamic data of the β-phase AgMg

At-% Mg	$E_{600°}$ mV	$\frac{dE}{dT}$ μV/1°	$-\overline{\Delta F^s_{Mg}}$ kcal	$\overline{\Delta S^s_{Mg}}$ cal/1°	$-\overline{\Delta H^s_{Mg}}$ kcal
420	205.5	−25	9.48	− 1.2	10.49
440	194.0	−28	8.95	− 1.3	10.08
455	197.9	−30	9.13	− 1.4	10.34
470	188.1	−27	8.68	− 1.3	9.77
481	184.5	−21	8.51	− 1.0	9.36
493	170.8	− 6	7.88	− 0.3	8.12
505	167.9	+ 7	7.75	+0.3	7.47
513	165.7	+20	7.64	+0.9	6.83
517	165.3	+30	7.63	+1.4	6.42
524	159.8	+32	7.37	+1.5	6.08
542	152.0	+40	7.01	+1.9	5.40
567	144.0	+37	6.64	+1.7	5.15
574	143.6	+36	6.62	+1.7	5.17
611	134.3	+33	6.20	+1.5	4.87

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REFERENCES

[1] K. W. Andrews, H. E. Davies, W. Hume-Rothery, C. R. Oswin, Proc. Royal Soc. A **177** (1941), 149.
[2] A. Oelander, Z. phys. Chem. A **165** (1933), 65.
[3] M. Straumanis, J. Weerts, Metallwirtschaft **10** (1931), 919.
[4] G. J. Petrenko, Z. anorg. Chem. **149** (1925), 395; **184** (1929), 376.
[5] A. J. Bradley, J. Thewlis, Proc. Royal Soc. A **112** (1926), 678.
[6] O. Kubaschewski, Z. phys. Chem. A **192** (1943), 292.
[7] C. E. Birchenall, C. H. Cheng, J. Metals **1** (1949), 428.
[8] N. W. Ageev, W. G. Kuznecov, Izw. Ak. Nauk SSSR, Ser. chim. (1937), 289.
[9] H. R. Letner, S. S. Sidhu, J. Applied Physics **18** (1947), 833.
[10] N. W. Ageev, Izv. Sektora Fiz-Chim. Analiza **16** (1943), 119.
[11] W. I. Smirnov, N. S. Kurnakov, Z. anorg. Chem. **72** (1911), 31.
[12] A. Oelander, J. Am. Chem. Soc. **54** (1932). 3819.

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CHEMISTRY

On the Anti-Tubercular Properties of Some Derivatives of Benzoxazine-1,3

by

T. URBAŃSKI, D. GÜRNE, Z. ECKSTEIN and S. ŚLOPEK

Communicated by T. URBAŃSKI at the meeting of May 16, 1955

In 1951, T. Urbański and S. Ślopek published a paper [1] on the anti-tubercular properties of a number of nitroparaffin derivatives, and particularly of derivatives of 5-nitro-tetrahydro-1,3-oxazine [2]-[7].

One of the compounds — 5-nitro-5-ethyltetrahydro-1,3-oxazine hydrochloride (designated as *T* 41) — showed an action similar to that of streptomycin against experimental TB in mice. However, a toxic action was observed upon prologned administration of the product. The toxic action may be produced by the presence of a nitro-group, and this led us to look for less toxic derivatives of 1,3-oxazine and to subject them to examination as anti-tubercular agents.

Thus, a number of derivatives of 4,4,6-trimethyl-tetrahydro-1,3-oxazine were recently prepared by T. Urbański and B. Chylińska [8]. (A number of compounds belonging to this group were originally obtained by M. Kohn [9]).

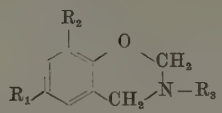
As shown by S. Ślopek, some of these compounds possess a moderate, although unquestionably bacteriostatic, action *in vitro* against *Mycobacteria*.

Continuing further this line of research, the authors of the present paper prepared a number of derivatives of benzoxazine-1,3, which form a group of compounds known since 1900 [10]-[13] and which have recently been examined by a number of authors, particularly Burke and his coworkes [14]-[18], from the point of view of the reactions leading to phenol-formaldehyde resins.

The following are the benzoxazine-1,3 derivatives prepared by the authors of the present paper (Table I).

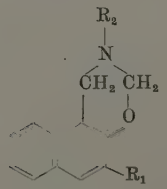
Products (1) and (2) have been described by Burke. The rest are new to the literature. The derivatives of naphtoxazine are shown in

TABLE I



No.	Name	R_1	R_2	R_3	Free bases m. p. °C.	Hydrochloride m. p. °C	Analysis				References
							Calculated		Found		
							% N	% Cl	% N	% Cl	
1	*T* 339	–Br	–	$-C_6H_{11}$	92–93	240–243					[6]
2	*T* 346	$-CH_3$	–	$-CH_2C_6H_5$	79–80	110–112					[6]
3	*T* 340	–Br	–	$-CH_2C_6H_5$	85–87	182–184	4.1	10.4	4.2	10.1	
4	*T* 348	–Br	–	$-C_2H_5$	–	171–172	5.0	16.6	5.2	17.0	
5	*T* 375	$-CH_3$	–	$-C_6H_{11}$	30–32	210–212	6.1	12.7	6.4	12.3	
6	*T* 379	–	$-OCH_3$	$-C_6H_{11}$	54–56	150–153	5.6	12.5	5.8	12.3	

TABLE II



No.	Name	R_1	R_2	Free bases m. p. °C	Hydrochloride	Analysis		References
						Calculated	Found	
						% N	% N	
1	*T* 356	H	$-CH_3$	67–68	190–193			[6]
2	*T* 378	H	$-C_6H_4COOH$	215	–			[6]
3	*T* 380	–COOMe	$-CH_2C_6H_5$	106–107	–	4.0	4.3	

TABLE III

Name	Bacteriostatic concentration			Lethal dose DL_{50} per os
	Myc. 297	*Smegm.*	H_{37} Rv	
T 339	3.9	7.8	7.8	3 g./kg.
T 346	31	31	31	–
T 356	7.8	15.5	15.5	–
T 340	3.9	7.8	3.9	3 g./kg.
T 348	62	31	15.5	–

Table II. Compounds (1) and (2) have also been described by Burke. Table III gives the bacteriostatic concentrations of some of the compounds *in vitro* against saprophytic *Mycobacteria*, which have been determined by one of us (S. Ślopek).

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REFERENCES

[1] T. Urbański and S. Ślopek, Nature **163** (1951), 562.
[2] E. L. Hirst. J. K. N. Jones, S. Minahan, F. W. Ochyński, A. T. Thomas, T. Urbański, J. Chem. Soc. (1947), 924.
[3] T. Urbański and E. Lipska, Roczniki Chem. **26** (1952), 182.
[4] T. Urbański and D. Gürne, Roczniki Chem. **28** (1954), 175.
[5] T. Urbański and J. Kolesińska, Roczniki Chem. **29** (1955).
[6] T. Urbański and H. Piotrowska, Roczniki Chem. **29** (1955).
[7] Z. Eckstein, W. Sobótka, T. Urbański, Roczniki Chem. **29** (1955).
[8] T. Urbański, B. Chylińska, Roczniki Chem. (in the press).
[9] M. Kohn, Monatsh. **25** (1904), 817, 850.
[10] M. Betti, Gazz. chim. ital. II, **30** (1900), 310; I, **31** (1901), 377; I, **33** (1903), 17; J. Chem. Soc. **80** (1901), 81, 611; **84** (1903), 510.
[11] M. Betti, A. Toricelli, Gazz. I., **33** (1903), 1; J. Chem. Soc. **84** (1903), 480.
[12] M. Betti, V. Foa, Gazz. I., **33** (1903), 27; J. Chem. Soc. **84** (1903), 511.
[13] N. Ahmed, N. G. Hemphill, F. E. Ray, J. Am. Chem. Soc. **56** (1934), 2403.
[14] W. J. Burke, J. Am. Chem. Soc. **71** (1949), 609.
[15] W. J. Burke, M. J. Kolbezen, C. W. Stephens, J. Am. Chem. Soc. **74** (1952), 3601.
[16] W. J. Burke, R. J. Reynolds, J. Am. Chem. Soc. **76** (1954), 1291.
[17] W. J. Burke, K. C. Murdock, G. Ec., J. Am. Chem. Soc. **76** (1954), 1677.
[18] K. G. Mizucz, J. Gen. Chem. (U. S. S. R.) **23** (1953), 861.

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CHEMISTRY

The Adsorption Microelectrode as an Indicator of Halogens in the Atmosphere

by
B. KAMIEŃSKI and J. KULAWIK

Presented by B. KAMIEŃSKI on May 19, 1955

A minute indicator electrode may be obtained by decreasing the volume of an electrolyte between two electrodes. A microelectrode was made [1] by melting a thin platinum wire (0.2 mm. in diameter) into a glass rod and then grinding and polishing the end. The area of a cross-section of the platinum wire was $0.1^2 \cdot \pi = 0.014$ mm^2. It should be emphasized here that a wire 0.01 mm. thick acts quite adequately in spite of the fact that its surface is 400 times smaller [2]. The ground rod was covered by a thin layer of silica gel and this layer was brought into contact with a minute calomel electrode. The thin layer of silica gel acts as an electrolyte; it separates the cross-section of the wire electrode from the surrounding atmosphere. Traces of atmospheric contamination are adsorbed by the gel, they diffuse through it to the platinum surface and change the potential of the electrode. The device is very sensitive to different gases [3] such as e. g., oxygen, hydrogen, hydrogen sulphide and others. Traces of various gases, tobacco smoke and smells of spices are adsorbed, and they change the potential of the platinum electrode.

Some active gases leave permanent products of the reaction with water contained in the gel or even with platinum. Others may be desorbed e. g., hydrogen or oxygen. The sensibility of the adsorption electrode requires that the atmosphere in the laboratory be kept exceptionally pure in order to establish a constant potential. Adsorbents were used (active charcoal) to purify the air but no constant potentials were obtained. Active charcoal appears to contain different substances, adsorbed occasionally from the cork or from the laboratory air, and these are eluted into the air gradually; this fact is an interesting one, suggesting the application of the electrode for chromatographic analysis of gases. However, in this paper it is another subject which is the main point of interest, namely, how to protect the element from contaminations and stabilize the "Zero" as accurately as possible. Drawing air through a piece of cotton-

wool from the air reservoir of the adjoining park by means of an aspirator appeared the best way.

The adsorption element is very sensitive to traces of halogens in the air and this could find some application in factory halls. We therefore studied the influence of halogens on the potential of the electrode. The potential ought to be measured by applying suitable quadrant or binant electrometers, the internal electrical resistance being very great. The following experiment may serve as an illustration of the performance of the device; chlorine was prepared electrolytically in a small electrolyser (2 ccm.), a platinum wire anode was applied, and a saturated sodium chloride was used as an electrolyte. A very weak electrical current of 0.045 mA was applied and traces of evolved chlorine were mixed steadily with a measured volume of air. The chlorine content was calculated from Faraday's law and after being thoroughly mixed by a system of tiny glass aspirators it passed along the silica gel layer of the microelement. Fig. 1 represents the results of the measurements. The potential of the element was 80 mV in fresh air. After applying the air-chlorine mixture (the arrow in the diagram) which was composed of 0.00007% of chlorine in air, a sudden change was observed in the potential which became reasonably constant at 164 mV for a period of 30 minutes. The possible losses of chlorine by adsorption on the walls of the glass container were not taken into account because of the constant flow of fresh portions of the gas mixture so that any losses were compensated for. When greater concentrations of chlorine were applied, further great changes in the potential were observed. However, the potential change became irreversible. The method of preparing the halogen was also changed when applying mixtures of greater chlorine content. In this case the chlorine was drawn from a reservoir; the gases were mixed in calibrated glass vessels and the mixture passed along the adsorption electrode.

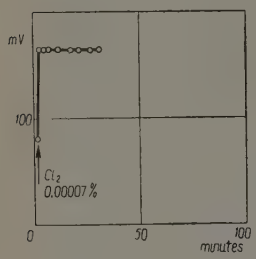

Fig. 1.

Fig. 2 represents the influence of chlorine at greater concentrations. When the concentration in air was 0.024%, the potential changed from 90 mV (in fresh air) to 824 mV. A further tenfold increase in the concentration (to 0.24%) did not cause great potential changes. The electrode reached 880 mV. Still another tenfold increase in the concentration resulted in an unexpected decrease in the potential and this phenomenon became more manifest at still greater concentrations. These negative changes in the potential are proof of a progressive chemical reaction at the surface of the platinum. Evidently, chlorine is bound by reaction more readily than it diffuses through the silica layer. If this assumption were right, it would be impossible to wash out the solid products of reaction by a stream

of fresh air. Actually, the solid compounds of chlorine and platinum remain on the electrode; fresh air was aspirated along the electrode for

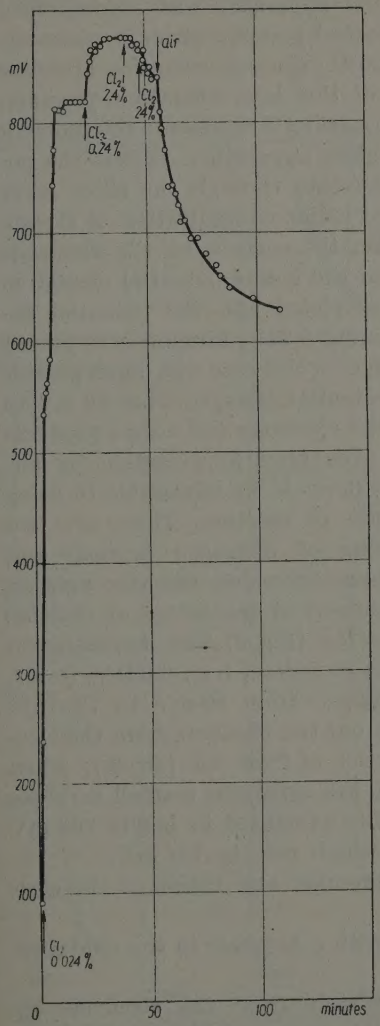

Fig. 2.

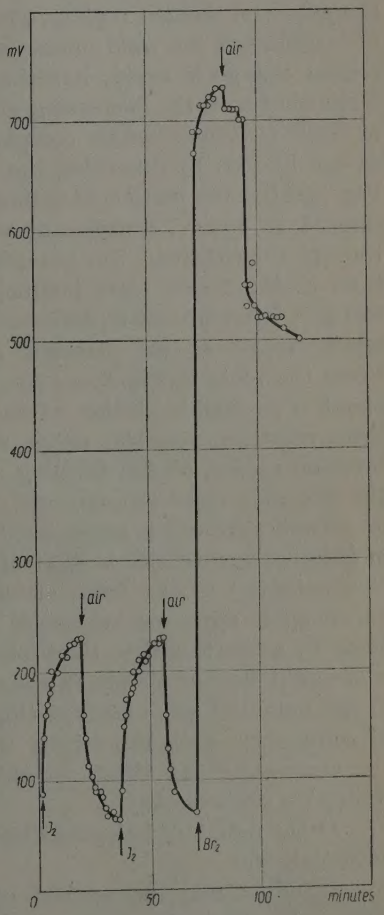

Fig. 3.

an hour and the potential never returned to its initial state and barely decreased to 625 mV.

The difference in the behaviour of iodine, bromine and chlorine in relation to the platinum electrode becomes clear when we compare the potential changes accompanying the application of similar concentrations of iodine, bromine and chlorine as shown in Fig. 3. The concentra-

tion of iodine in air was 0.024% and similar concentrations of bromine and chlorine were applied in the next experiments, shown in Fig. 3. The introduction of solid iodine into the apparatus was accompanied by a potential change of 138 mV. The partial pressure of iodine amounts to c. 0.18 mm. Hg at a temperature of 20°C.; the concentration of iodine thus becomes 0.024% in air. In spite of this low saturation pressure, the potential changes rapidly. The arrow marked *I* represents the moment of introducing the solid iodine into the glass apparatus. At first the potential change is rapid, but the diffusion rate through the silica layer diminishes with the decreasing gradient of iodine concentration. A stream of fresh air elutes iodine completely from the surface of the electrode as can be seen by observing the course of the iodine potential change in Fig. 3. After the elution of iodine was completed and the potential decreased to 60 mV, a stream of air containing 0.24% bromine was passed through the electrode. The potential change in this case was much greater than in the former case (iodine); the potential changed from 60 mV to 580 mV. Bromine reacts, however, with the electrode and forms products which remain on the platinum surface even after long elution by air. From the plots in Fig. 3 one can see that it would be impossible to bring about a reversible elution of the products of reaction. There are two main reactions possible; either the forming of hydrogen bromide and bromine oxides, or the forming of platinum bromides. Chlorine acts on the electrode more strongly still. The moment of the action of chlorine on a fresh electrode is represented by an arrow (Fig. 3). The concentration of chlorine was similar to that of bromine or iodine, i. e., 0.024% in air. The potential of the fresh electrode changed from 90 mV to 724 mV, and it again appeared impossible to wash out the products from the electrode by subjecting it to the prolonged action of fresh air (arrow); when a constant flow of air was introduced into the apparatus a small decrease in the potential was observed (Fig. 3). This amounted to barely 206 mV in comparison with the former increase which rose to 724 mV.

Comparing the effects of chlorine, bromine and iodine on the electrode, we observe that

1) the action of halogens diminishes with a decrease in the oxidation potential, and

2) iodine may be washed out completely from the electrode by means of a stream of air, but it is impossible to remove the reaction products of bromine or chlorine from the platinum. The traces hydrogen iodine formed under the action of the water contained in the silica gel layer are unstable when air is applied as an eluent. It is reasonable to assume that oxygen (air) decomposes hydrogen iodide, forms iodine and elutes the halogen completely. On this assumption we conclude that it is impossible to elute the products of iodine by applying a gas which does not contain oxygen as an oxidizing factor.

In order to ascertain whether this conclusion is correct, the elution experiments were repeated, twice with iodine and air and once with bromine, as can be seen in Fig. 4. The process of adsorption and resorption

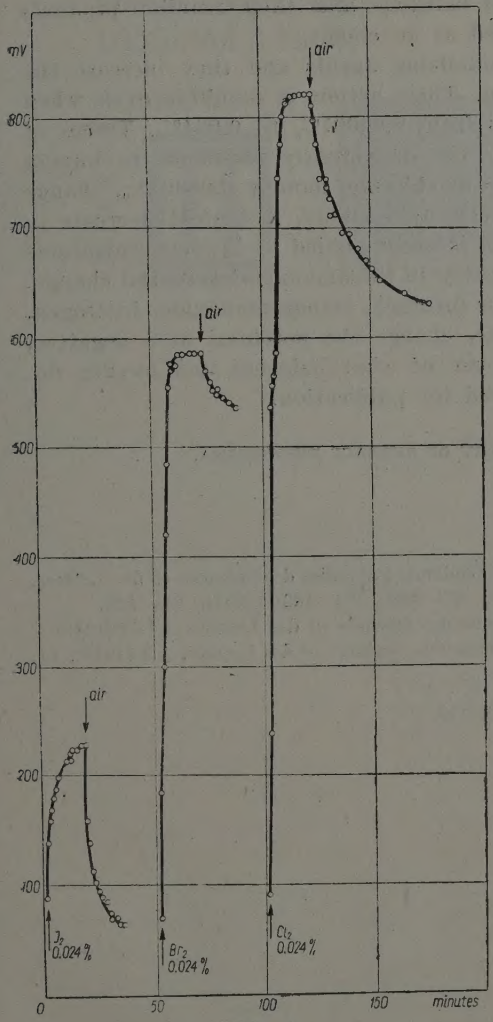

Fig. 4.

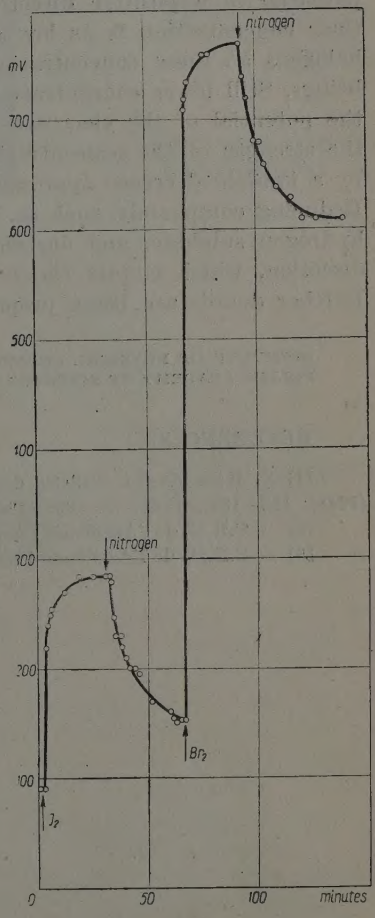

Fig. 5

is reversible with iodine but irreversible with bromine as can be seen in Fig. 4. The experiments were carried out with saturated iodine vapour (0.024%) and bromine vapour (24%). In the last experiment (Fig. 5) a stream of pure nitrogen was applied as an eluent instead of air. The arrows mark the respective moments of applying iodine (0.024%) and

nitrogen. As can be seen in Fig. 5, the potential did not return to its initial value either in the case of iodine or in that of bromine (24%). Comparing the action of nitrogen with that of air (oxygen) it can be seen that, as was concluded, the elution of halogens and their reaction products is more efficient when air is used as an eluent.

Halogens are very strong oxidizing agents and they increase the potential in a positive direction. Their action is manifest even when their concentration is as low as from 0.00007% to 0.024%. Traces of halogens at these concentrations are dangerously poisonous to human beings. Still lower concentrations of chlorine, namely 0.00001%, change the potential of the electrode quite appreciably. A tenfold decrease in the strength of the concentration is accompanied at low concentrations by a twofold decrease approximately in the amount of potential change. Reducing compounds, such as, for instance, carbon monoxide, hydrogen, hydrogen sulphide, and acetylene, change the potential in a negative direction, which is just the reverse of what halogens and oxygen do. Further details are being prepared for publication.

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REFERENCES

[1] B. Kamieński, Bulletin de l'Académie Polonaise des Sciences et des Lettres, (1948), 128–133; (1949), 75–89; (1949), 157–160, 171–182; (1951), 199–222.
[2] – C.R.M. de l'Académie Polonaise des Sciences et des Lettres, A **1–2** (1949), 7
[3] – C.R.M. de l'Académie Polonaise des Sciences et des Lettres, A **3** (1949), 14.